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OPTICAL STUDIES OF AUTOMOTIVE AND NATURAL HAZES: SCATTERING FROM SINGLE PARTICLES

(FINAL REPORT)

Authors

David T. Phillips, Ph.D.
Philip J. Wyatt, Ph.D

Supported by

Environmental Protection Agency
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Science Spectrum, Inc.
Santa Barbara, California

February 1971

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The objective of this study was to determine the feasibility of using measurements of the angular variation of the intensity of light scattered from single particles in the problem of identifying haze or aerosol particles originating from auto exhaust emissions. Scattering measurements were to be on single "smog" particles during a period of haze in Los Angeles. Analysis of scattering curves for larger laboratory aerosol particles shows measurable differences in refractive index between a photochemical pine tree aerosol and a photochemical petroleum aerosol. For particles of diameter less than 500 nanometers only the measurement of absolute scattering intensity at two angeles is required. Distinctive non-spherical and absorbin g particles were observed both in automotive exhaust and atmospheric samples. Field measurements of single particle light scattering were carried out in Los Angeles and Santa Barbara.

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ABSTRACT

The use of single particle light scattering measurements to determine the origin of atmospheric hazes has been explored by measurement of laboratory aerosols, field samples, and computer analysis of the light scattering data.

Analytical methods are developed for the determination of refractive index of such particles.

Analysis of scattering curves for larger laboratory aerosol particles shows measurable differences in refractive index between a photochemical pine tree aerosol and a photochemical petroleum aerosol. For particles of diameter less than 500 nanometers only the measurement of absolute scattering intensity at two angles is required. Distinctive non-spherical and absorbing particles were observed both in automotive exhaust and atmospheric samples. Recommendations are made for further development and testing of the single particle optical scattering method for particulate air pollution analysis.

ACKNOWLEDGMENTS

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1. INTRODUCTION

This project is a part of the continuing joint haze research effort of the Air Pollution Control Office and the Coordinating Research Council, Inc. A recent review of work in this area was given by O. A. Germogenova, et al, in *Atmospheric Haze: A Review*, Bolt, Beranek and Newman, Report No. 1821, March 1970, a Final Report for Contracts CAPA-6-68 (1-68) and CPA 22-69-29.

A specific impetus for the focus of the present project on the difference between petroleum and vegetative based haze is the work by R. A. Rasmussen of Washington State University, Pullman, Washington, on the contributions of trees to air pollution. An exhaustive discussion of light scattering and its applications may be found in the book by M. Kerker, *The Scattering of Light and Other Electromagnetic Radiation*, Academic Press, New York 1969.

Objective.

The objective of this study was to determine the feasibility of using measurements of the angular variation of the intensity of light scattered from single particles in the problem of identifying haze or aerosol particles originating from auto exhaust emissions. Particles to be examined included reaction chamber products produced by the following reactions:

1) Auto exhaust + NO_2 + UV radiation

2) Pine tree limbs + NO_2 + UV radiation

Scattering measurements were to be attemped on single "smog" particles during a period of haze in Los Angeles.

Results.

Measurements of the angular variation of light scattered from single particles produced in a reaction chamber by the reactions,

1) Gasoline + NO_2 + UV radiation

2) Pine cone + NO_2 + UV radiation,

show that these aerosols can be distinguished by single particle light scattering measurements. The refractive index of a petroleum aerosol particle was found to be 1.54 ± 0.02 while the pine aerosol particle index was 1.49 ± 0.01. No attempt was made to accurately reproduce atmospheric conditions in those laboratory experiments.

Field measurements of single particle light scattering were carried out in Los Angeles and Santa Barbara. During the period available for field measurements pollutant levels were not high enough to cause eye irritation, though visibility was reduced to 4-12 miles by photochemical haze. Haze particles measured ranged from 200 nm (nanometers) to 500 nm in diameter.

A method by which the refractive index of particles of diameter 100 to 500 nm can be determined using measurements of the absolute intensity of the scattered light in addition to its angular variation has been developed. The theoretical scattering computations required for the method have been carried out.

Nonspherical particles, identified by flicker in the scattered light, were found both in fresh samples of auto exhaust and field samples of atmospheric haze.

Recommendations.

The feasibility of single particle optical determinations of refractive index has been demonstrated for specific laboratory aerosols. Field measurements show the method can be applied to atmospheric haze. Single particle optical measurements promise to be useful for study and control of particulate atmospheric contamination. Further testing and development of the optical method is required.

Precise measurement of absolute scattering intensity together with the angular dependence of scattering should be employed to determine the refractive index of small particles. Depolarization, flicker, and dissymetry measurements should be investigated in connection with nonspherical particles. Further analytical studies are needed for these particles. Analysis of scattering from absorbing metallic or combustion products should be carried out. Optical field studies should be made routinely in Los Angeles as well as measurements in contrasting rural and urban areas. Joint chemical and optical studies, both in the laboratory and of the Los Angeles atmosphere are needed to aid the initial interpretation of optical data.

2. EXPERIMENTAL PROGRAM

Laboratory Aerosol Production.

Four different laboratory aerosols have been produced in a ten-gallon glass chamber. In each case, a 40-watt quartz envelope-mercury discharge lamp was used as a source of ozone and ultraviolet radiation. NO_x was generated for some experiments by dropping a few strands of copper wire into a 40% solution of nitric acid. The concentration of the reactants in these experiments were higher than those normally found in the atmosphere.

1. A handful of lemon leaves, crushed and placed in the chamber, quickly react with the ozone to produce a fine aerosol of spherical particles.

2. A large resin-laden pine cone placed in the chamber reacts with the ozone to produce a continuing supply of spherical aerosol particles.

3. Samples of auto exhaust, captured in plastic bags, cooled to remove excess moisture, and introduced into the chamber contained particles of irregular shape, which settled out in 24 hours. The low concentration of hydrocarbons in the exhaust sample prevented the growth of large particles in the small reaction vessel.

4. Raw gasoline in an open dish together with NO_x and ozone produced a heavy aerosol of spherical particles as well as a tarry deposit on the walls of the reaction chamber.

Differential II Instrument.

The Science Spectrum *Differential II* single particle scattering photometer was used to make the measurements described in this report. A schematic representation of a light scattering photometer is shown in Fig. 1. Samples of the aerosol were removed from the reaction chamber with a 50 cc syringe, and injected into the scattering cell in a slowly moving air stream. They can be viewed by eye as they cross a laser beam. Particles selected for study are held indefinitely in the cell by electrostatic fields. When the particle is first selected, the electric fields are varied under manual control to hold the particle near the center of the laser beam. Within a few seconds the particle chosen is pulled to the center of the cell by the radial component of the field, while other particles are swept away, because their charge-to-mass ratio and initial position are different than the particle selected for study.

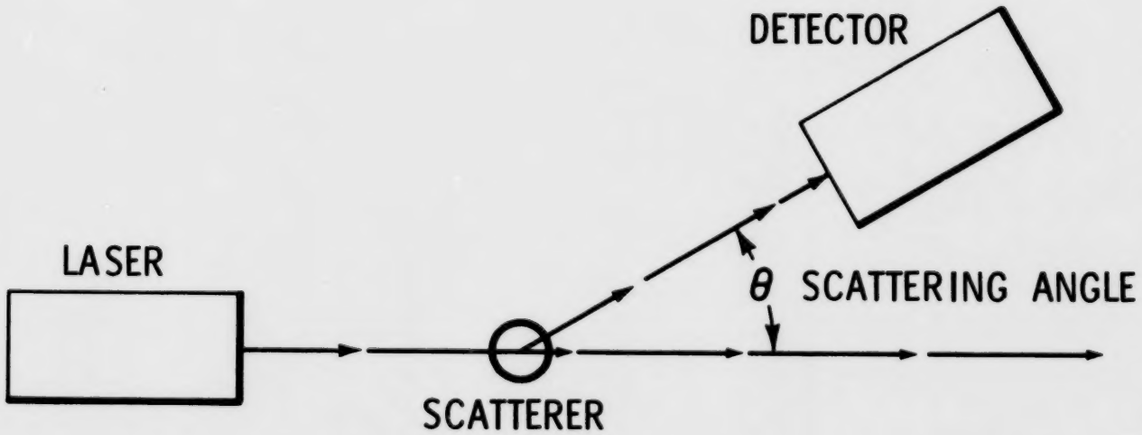


Figure 1 - Schematic representation of the light scattering measurement. Scattered light intensity is recorded as a function of scattering angle by the *Differential II* single particle photometer.

The electric charge of the laboratory aerosols was found to vary. To hold particles with only one or two electrons, electrode potentials were increased to 1000 volts. Aerosols formed with zero charge were charged with a 20 kv corona discharge electron gun.

When the chosen particle is alone in the beam, control of the fields is transferred to an automatic servo system which photoelectrically monitors the particle position. While the particle is held steady in the laser beam, a 1P21 photomultiplier detector with appropriate masks and filters is rotated around the cell. An X-Y recorder plots the scattered light intensity as a function of angle.

The light source is a Science Spectrum/TRW special pulsed argon-ion laser tunable to the following wavelengths:

Wavelength (nm)	Relative Intensity	Average Power (mW)
514.5	1.00	.5
496.5	.34	.17
488.0	.6	.3
476.5	.36	.18
457.9	.08	.04

The beam is single transverse mode, plane polarized, with 1 milliradian divergence.

Other characteristics of the *Differential II* are:

Angular Resolution (scattered light): 2.0°

Angular Incremental Advance: 2.5 minutes

Scanning Speeds: 180°/min., 90°/min., 45°/min., 22.5°/min., 11.3°/min.

Slewing Speed: 720°/min.

Angular Range: 8° to 172°

Angular Accuracy (readout) ± 40 minutes

Measurements of Laboratory Samples.

Plots of light scattering intensity versus scattering angle for single particles of reaction chamber aerosols are shown on the following pages. In all cases the light was plane polarized

and of wavelength 514.5 nm. The laser was mounted to provide vertically polarized light (perpendicular to the scattering plane) and a half wave plate was used to obtain horizontal polarization (parallel to the plane of scattering), without much loss of light intensity. The curves presented are the basis for the laboratory test of the feasibility of the use of single particle light scattering measurements to determine the origin of haze particles. The sensitivity of the instrument has been adjusted to place the first peak near the top of the scale.

Figure 2 shows the vertically and horizontally polarized light scattering patterns from a pine-ozone haze particle when first captured. Note that the vertical curve has six peaks. Figure 3 shows the vertical scattering from the same particle 90 minutes later. Evaporation has reduced the particle size and only five peaks remain. This vegetative particle is to be distinguished from the petroleum based particle whose vertical and horizontal polarization scattering curves are shown in Figure 4. The analysis of this data is discussed in Section 3.

Fresh auto exhaust samples, taken from an idling 50,000 mile Volkswagen sedan burning leaded regular gas was found to contain a large number of particles exhibiting a distinct forward peak in scattered light intensity. A typical measurement, shown in Figure 5, illustrates the steep forward peak and flicker characteristic of these particles. It is reasonable to suppose that these samples are mixtures of lead and solid combustion products like carbon, though chemical studies and theoretical analysis of the scattering from such objects have not been performed. Such particles are distinctive and may provide an indication of fossil fuel air contamination.

Field Studies.

For the field measurements a mobile laboratory was constructed. The *Differential II* photometer and its recorder were mounted on a table in the rear of an I. H. Scout vehicle. A portable power pack utilizing two lead-acid storage batteries and a 275 watt inverter was used for power. Though the voltage was reasonably stable, the supply was not regulated and absolute intensity calibration was not attempted. The operator was seated in the rear seat in a convenient position to operate the instrument. Extreme temperature variations caused some difficulty with optical alignment but not enough to prevent the use of the instrument. Hundreds of particles were visible in each sample. Haze particles with sufficient charge to hold were relatively infrequent, but enough were easily found for the measurements.

Figure 2 - Initial pine + UV particle differential scattering intensity. Vertical and horizontal polarizaton, incident wavelength 514.5 nm.

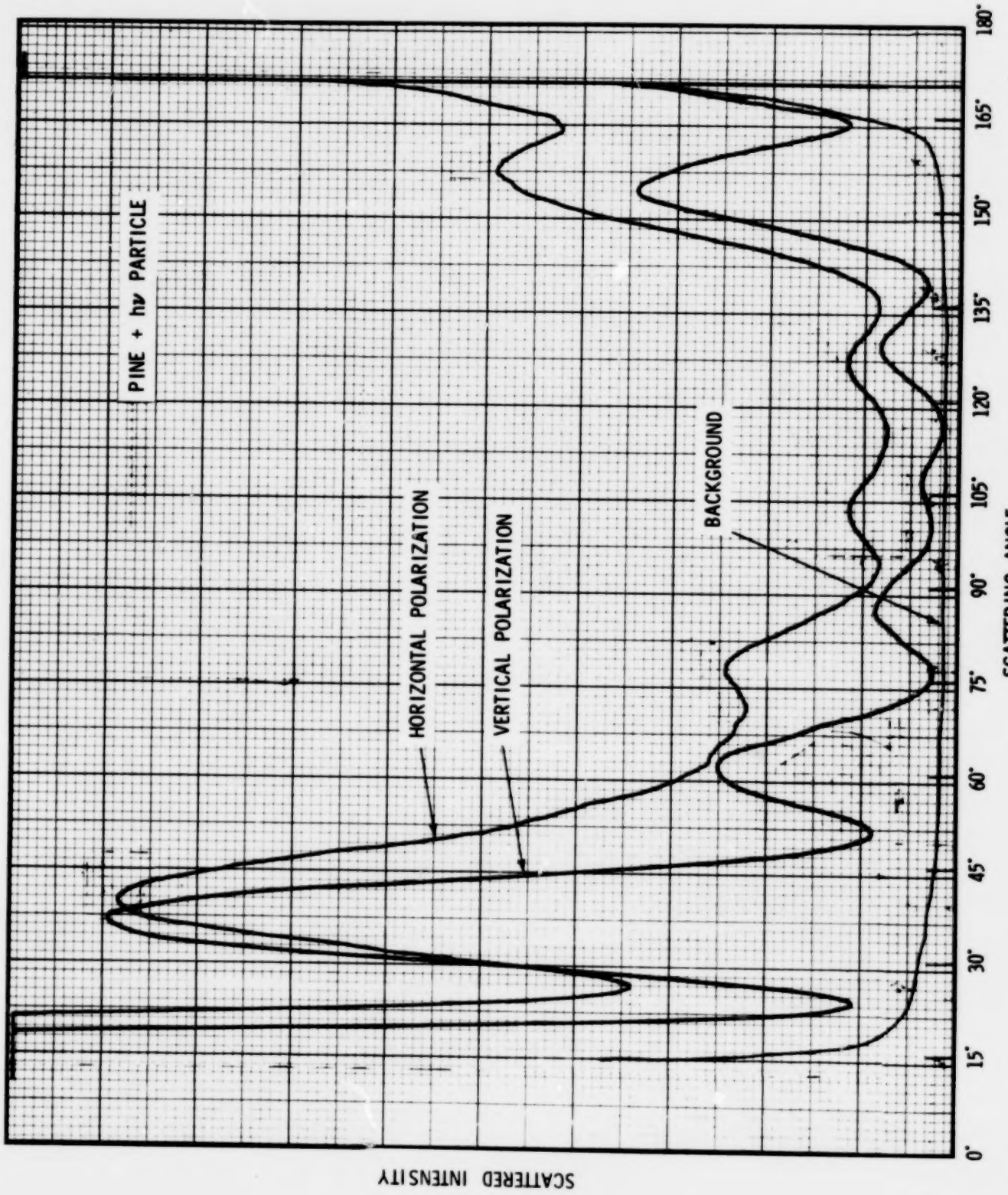


Figure 3 - Differential scattered intensity of a pine + UV particle after 90 minutes. Vertical polarization, 514.5 nm wavelength.

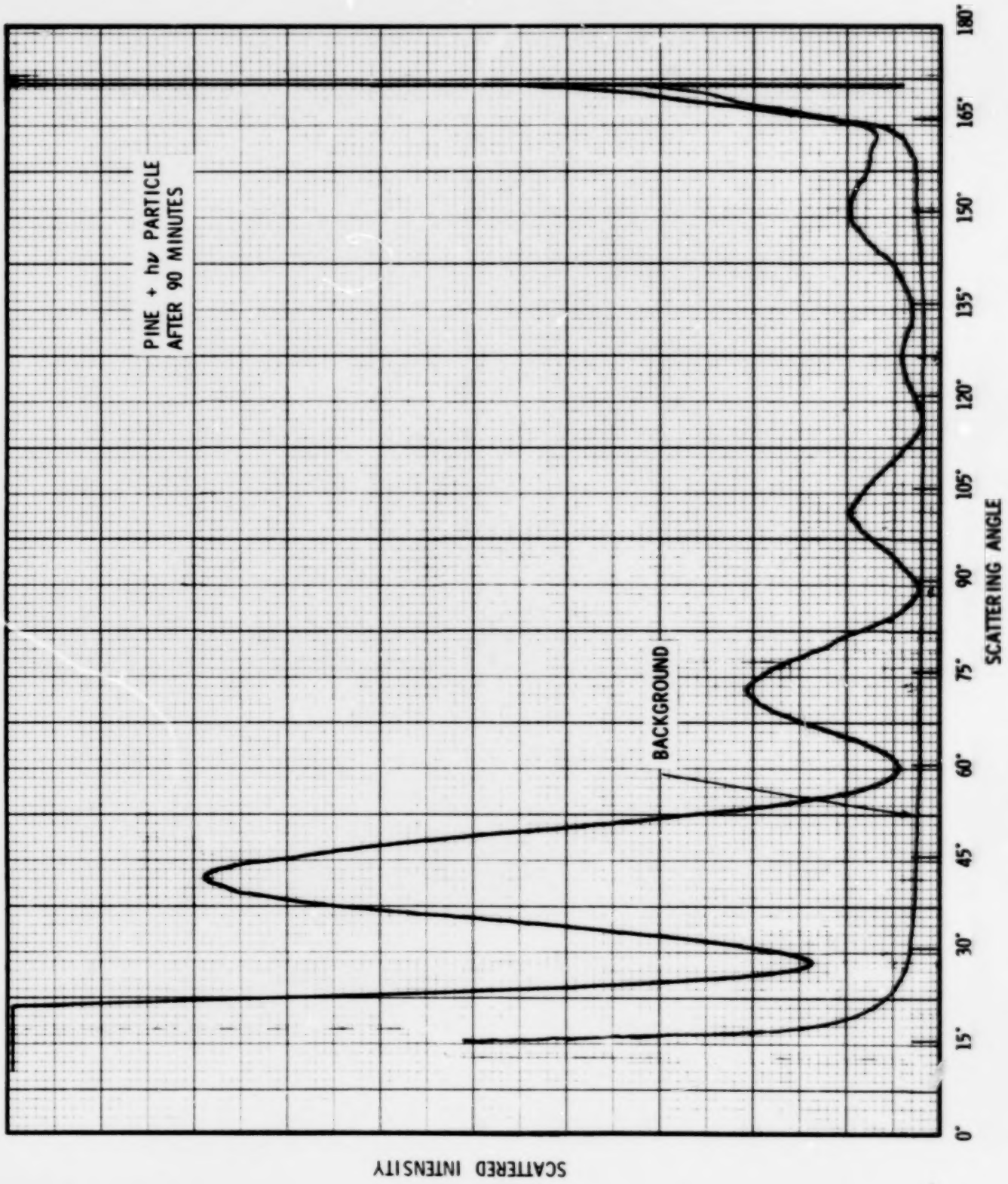


Figure 4 - Differential scattered intensity of a gasoline + NO_x + UV particle. Vertical and horizontal polarization 514.5 nm wavelength.

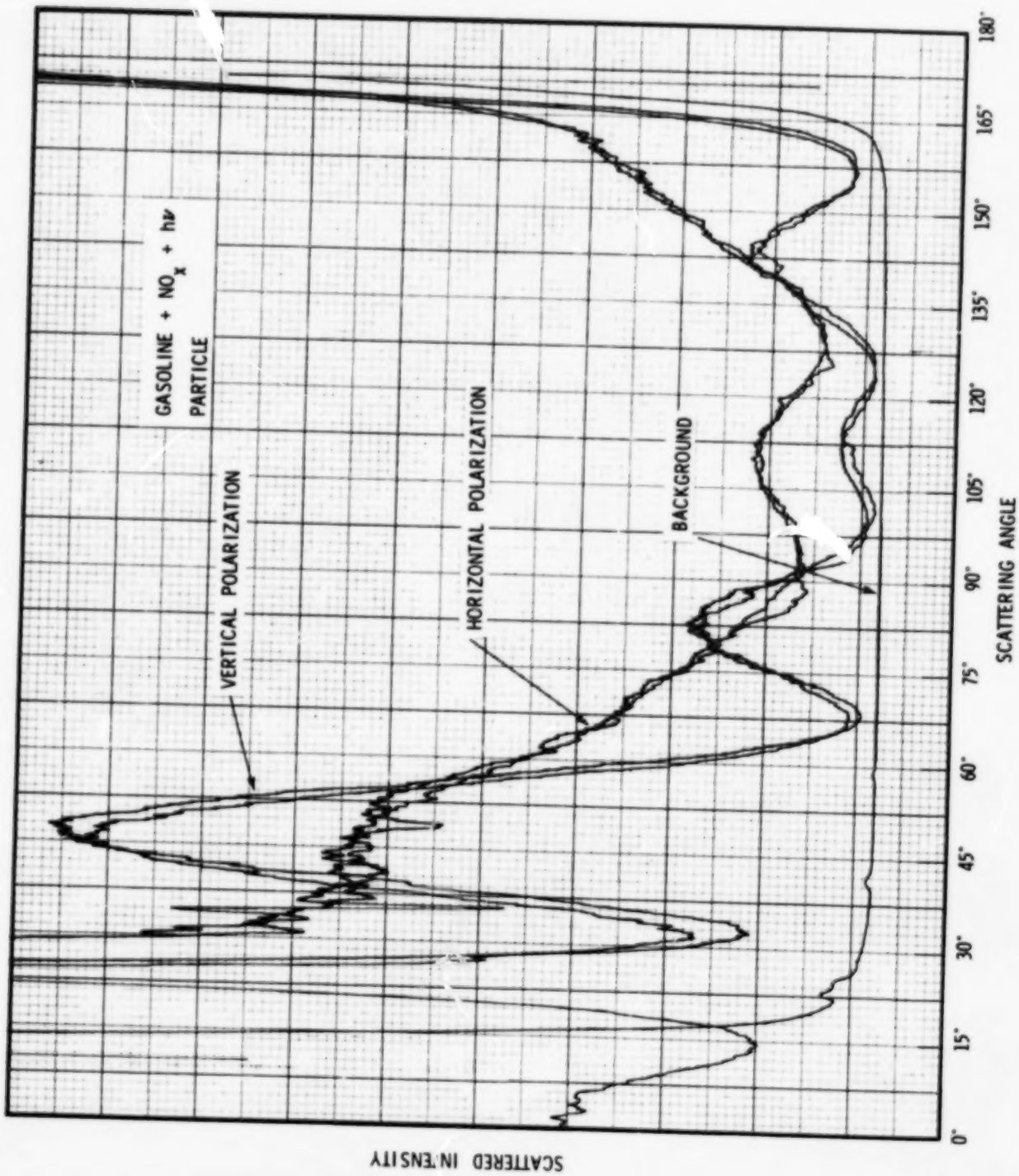
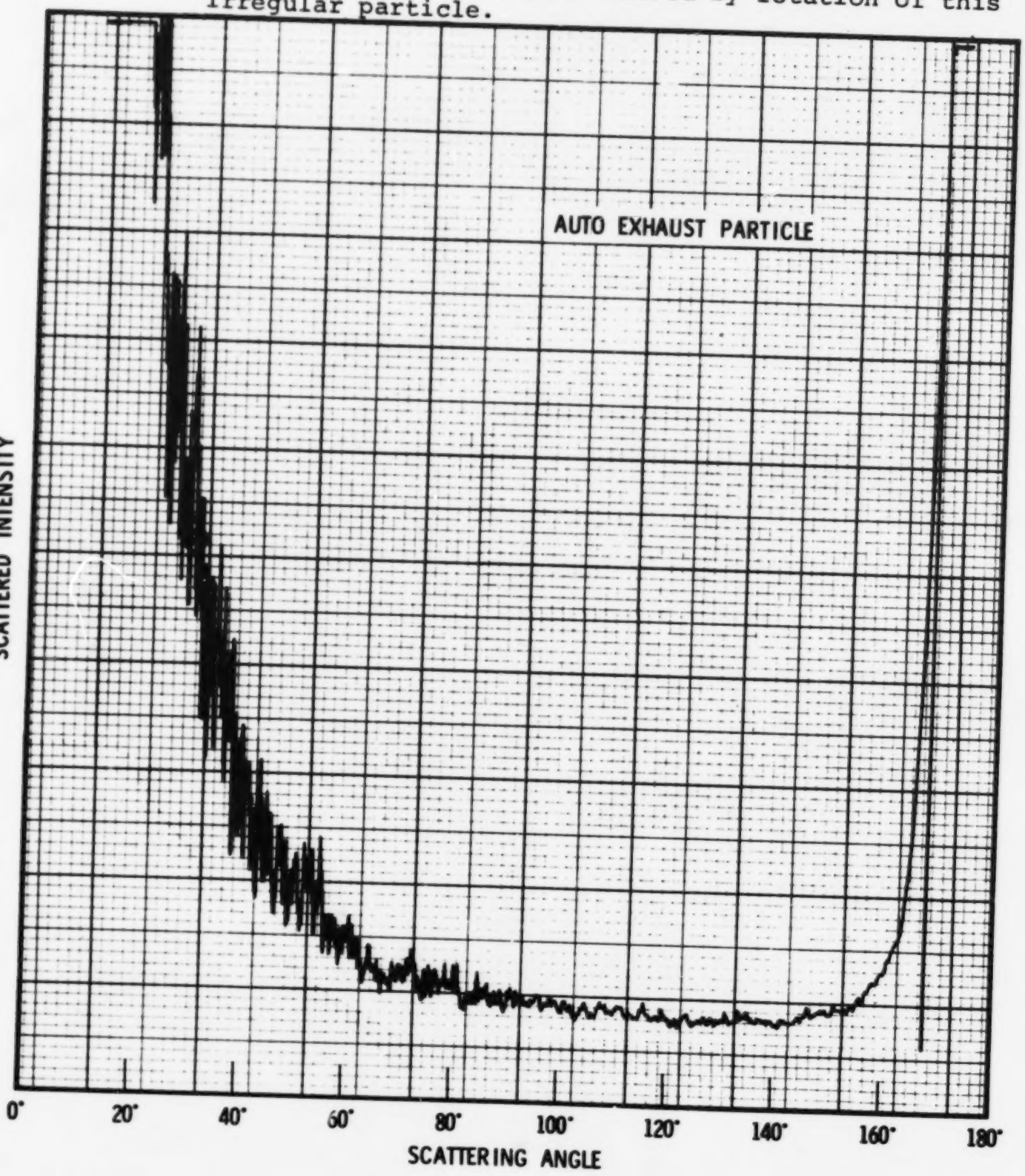


Figure 5 - Automobile exhaust particle differential scattered intensity, vertical polarization 514.5 nm wavelength. Note the signal variation caused by rotation of this irregular particle.



Field studies were made on January 25 through 31 in Santa Barbara, as well as 15 miles to the west in Goleta and 100 miles to the east in Los Angeles during light haze. No severe smog conditions occurred in Los Angeles during the period that the mobile laboratory was in operation. Measurements were made in Burbank and Universal City areas of Los Angeles on January 27 when visibility was limited to 6-12 miles by photochemical haze. No eye irritation was present. Typical scattering curves are shown in Figures 6 through 10. The size of the spherical haze particles observed was typically 500 nm or smaller, as determined by comparison with theoretical curves shown in Section 3. Figure 10 shows an atmospheric particle with fluctuations similar to those observed in automotive exhaust samples. The accurate optical classification of such irregular particles remains to be done, though precise measurement of the fluctuation amplitude is technically straightforward.

Figure 6 - Haze particle differential scattered intensity. Burbank (Los Angeles county). Vertical polarization 514.5 nm wavelength.

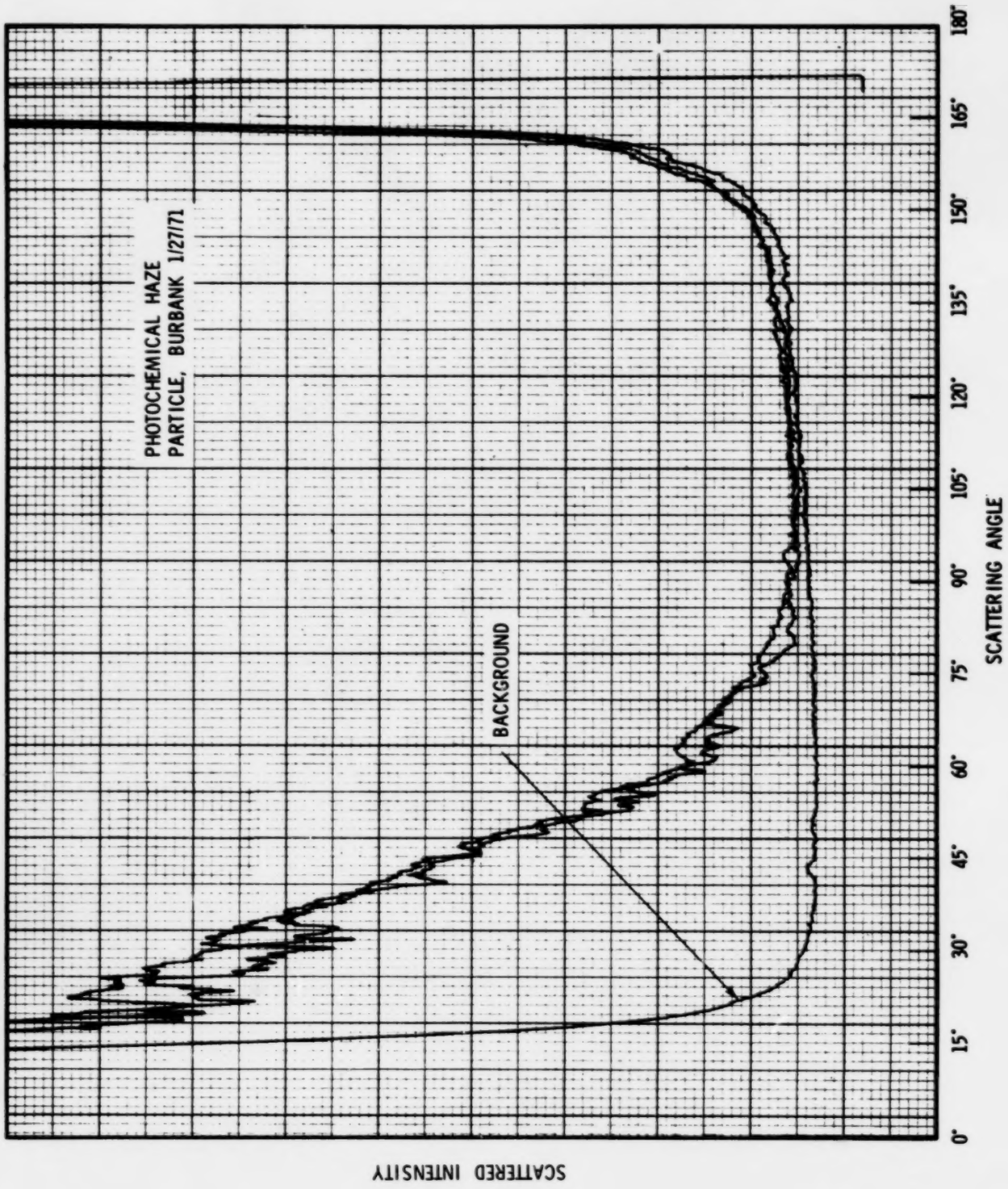


Figure 7 - Haze particle differential scattered intensity. Goleta (Santa Barbara county). Vertical polarization, 514.5 nm wavelength.

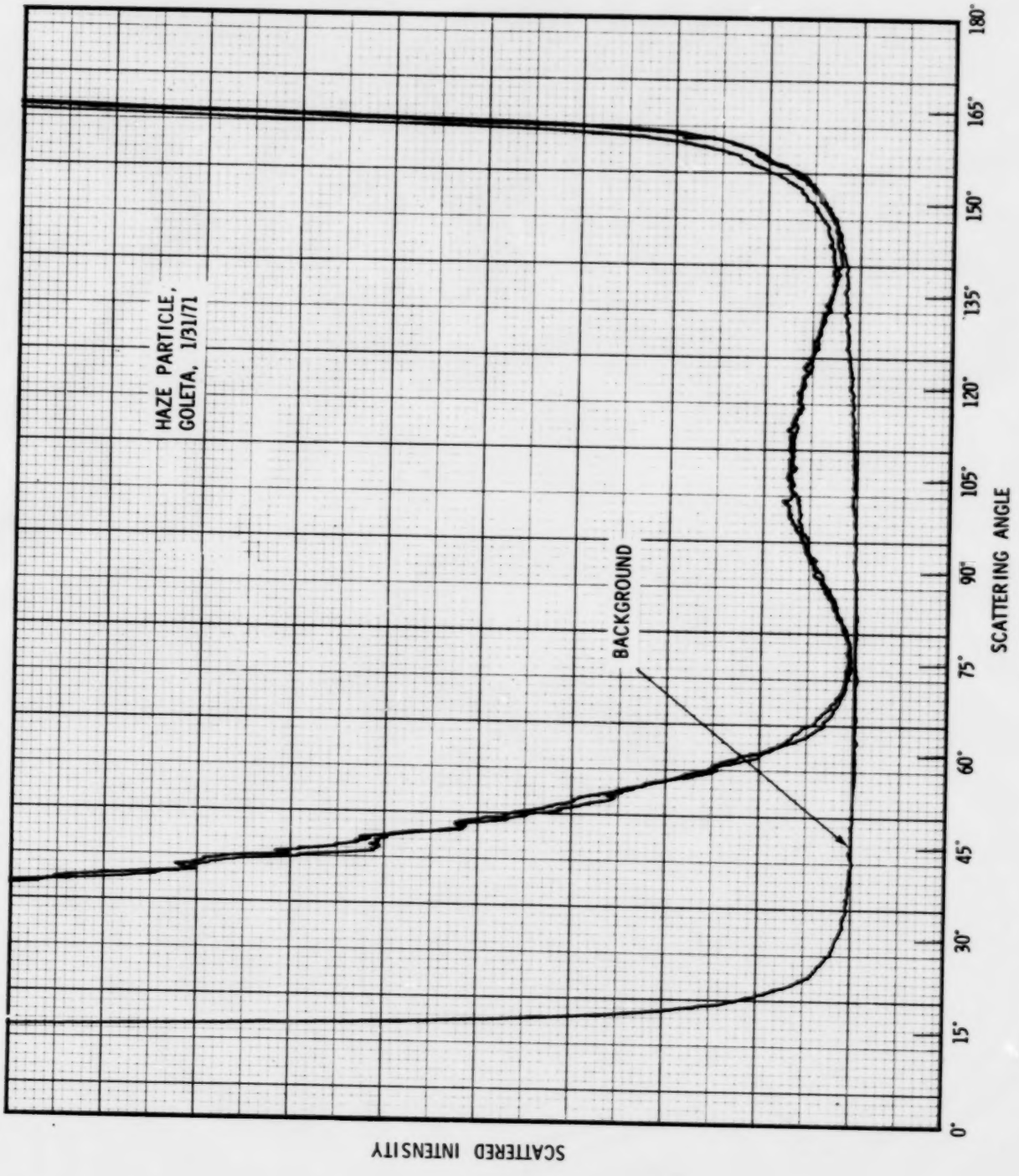


Figure 8 - Irregular atmospheric particle differential intensity, Santa Barbara. Vertical polarization, 514.5 nm wavelength. Note the similarity to the automobile exhaust particle shown in Figure 5.

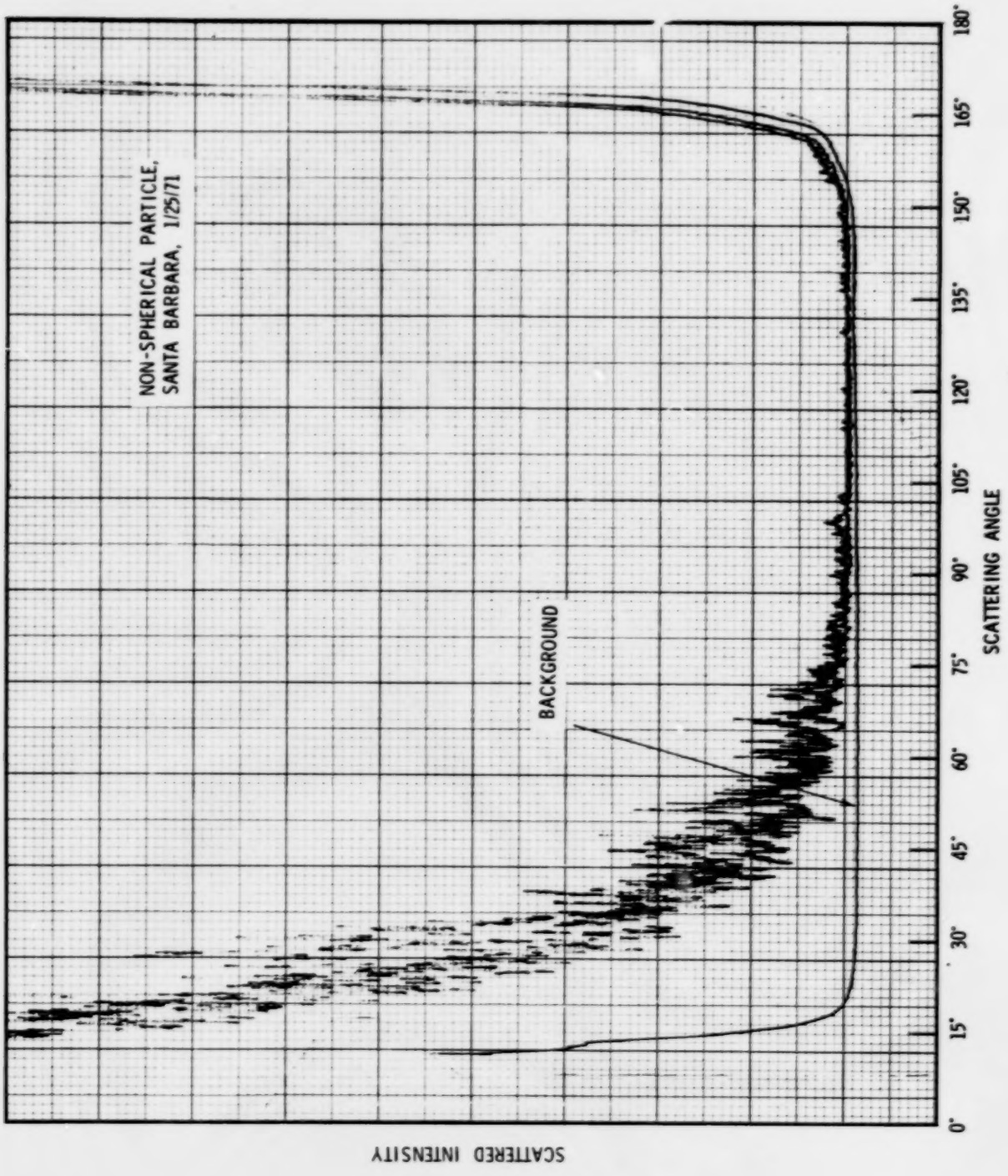


Figure 9 - Theoretical differential scattered intensity for homogeneous spherical particles of refractive indices 1.33, 1.42, 1.5, 1.59 at 514.5 nm wavelength. Particle diameter 100 nm, vertical polarization.

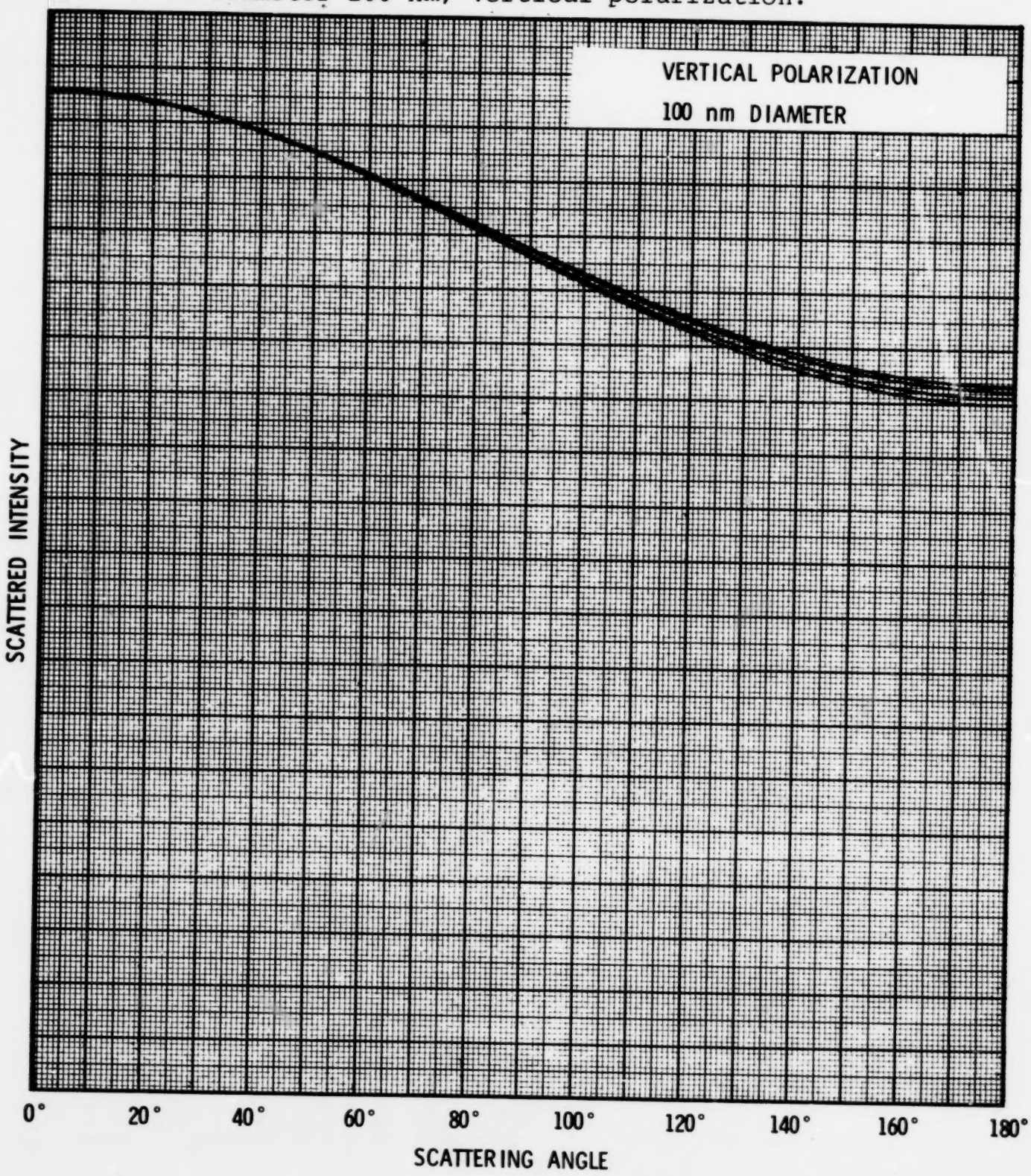
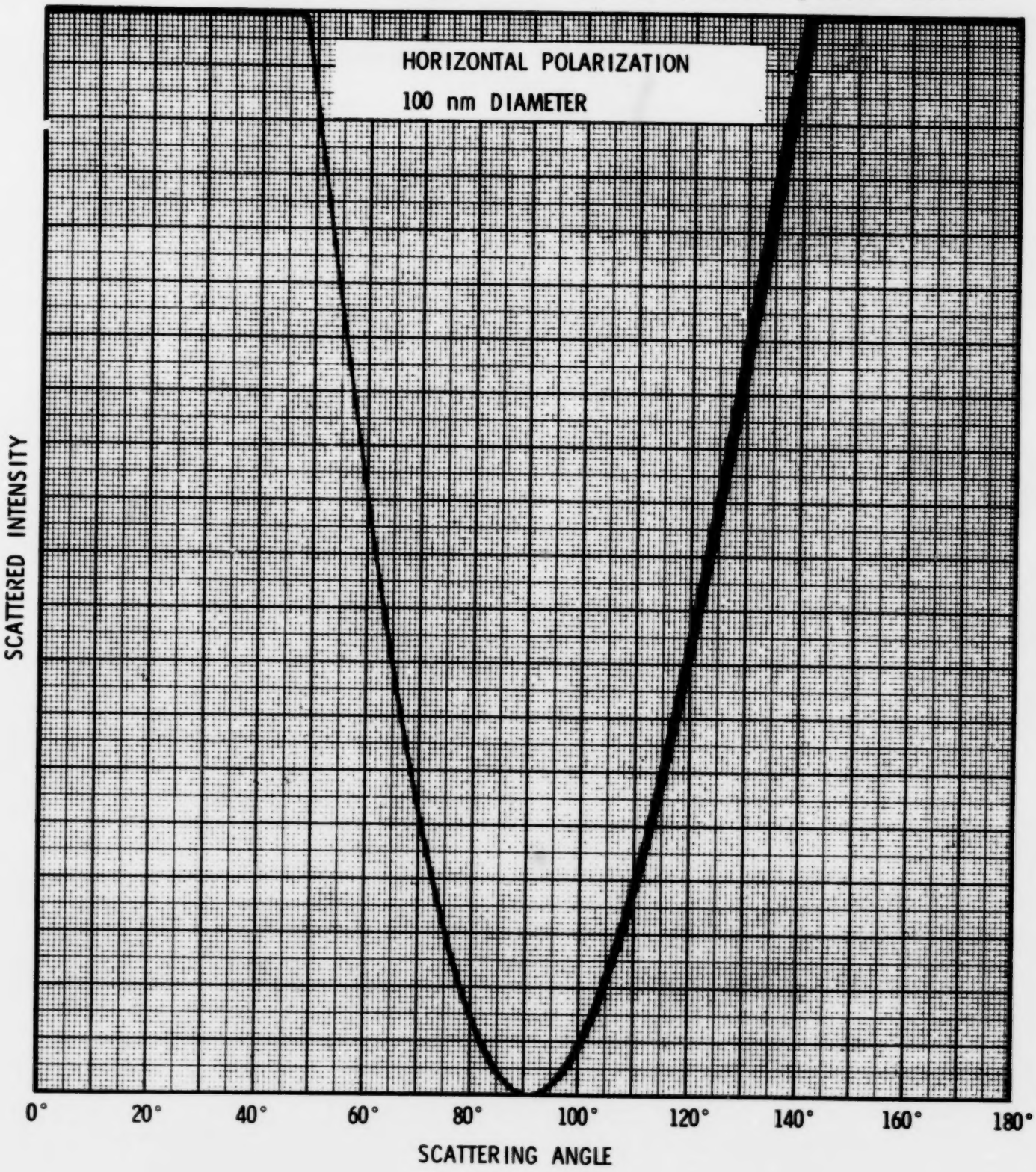


Figure 10 - Theoretical differential scattered intensity for homogeneous spherical particles of refractive indices 1.33, 1.42, 1.5, 1.59 at 514.5 nm wavelength. Particle diameter 100 nm, horizontal polarization.



3. ANALYTICAL PROGRAM: DEDUCTION OF SIZE AND REFRACTIVE INDEX

The objective of the analysis of the scattering data is to identify the source of the measured particle. Many of the particles seen appear to be spherical as evidenced by steady scattering, as would be expected from droplets of water or tarry liquids. In light scattering, spherical particles are characterized by their radius and refractive index. Though the radius of the particles may be of meteorological interest, the refractive index is a direct consequence of the chemical composition of the particle, and thus offers an important guide for identification. In this study the primary analytical problem has been the determination of refractive index from light scattering data.

Though most of the particles scattered light steadily, indicating spherical symmetry, some particles were seen to flicker violently. These may be particles with irregular shape such as combustion products composed of metals, carbon, or other absorbing materials. Such materials are common air pollutants. No attempt was made to analyze the scattering of nonspherical or absorbing particles, though the presence of such particles in fresh auto exhaust samples suggests they may provide important information in atmospheric studies.

Layered structures formed by the condensation of one material on a nucleus of a different material are also important in the formation of haze. No attempt was made to test the measured curves for the presence of such particles though this should be possible if the nucleus is 50 nm or larger in diameter.[1]

Extensive digital computer calculations have been used to quantitatively interpret the measured single spherical particle scattering curves. Theoretical scattering curves for vertically and horizontally polarized 514.5 nm wavelength light incident on homogeneous, transparent spheres of diameter 100 nm, 300 nm, 500 nm and 1000 nm with refractive index 1.33 (water), 1.42 (protein), 1.5 (glass), 1.59 (latex), are given in Figs. 11 through 18.

Note that the numbers of peaks in the vertical scattering curve is given approximately by $2Dn/\lambda$, which provides a simple way to size particles within about 0.1 micron. Note also that the curves for particles with higher refractive index tend to have variations of larger relative amplitude in the back angles.

Figure 11 - Theoretical differential scattered intensity for homogeneous spherical particles of refractive indices 1.33, 1.42, 1.5, 1.59 at 514.5 nm wavelength. Particle diameter 300 nm, vertical polarization.

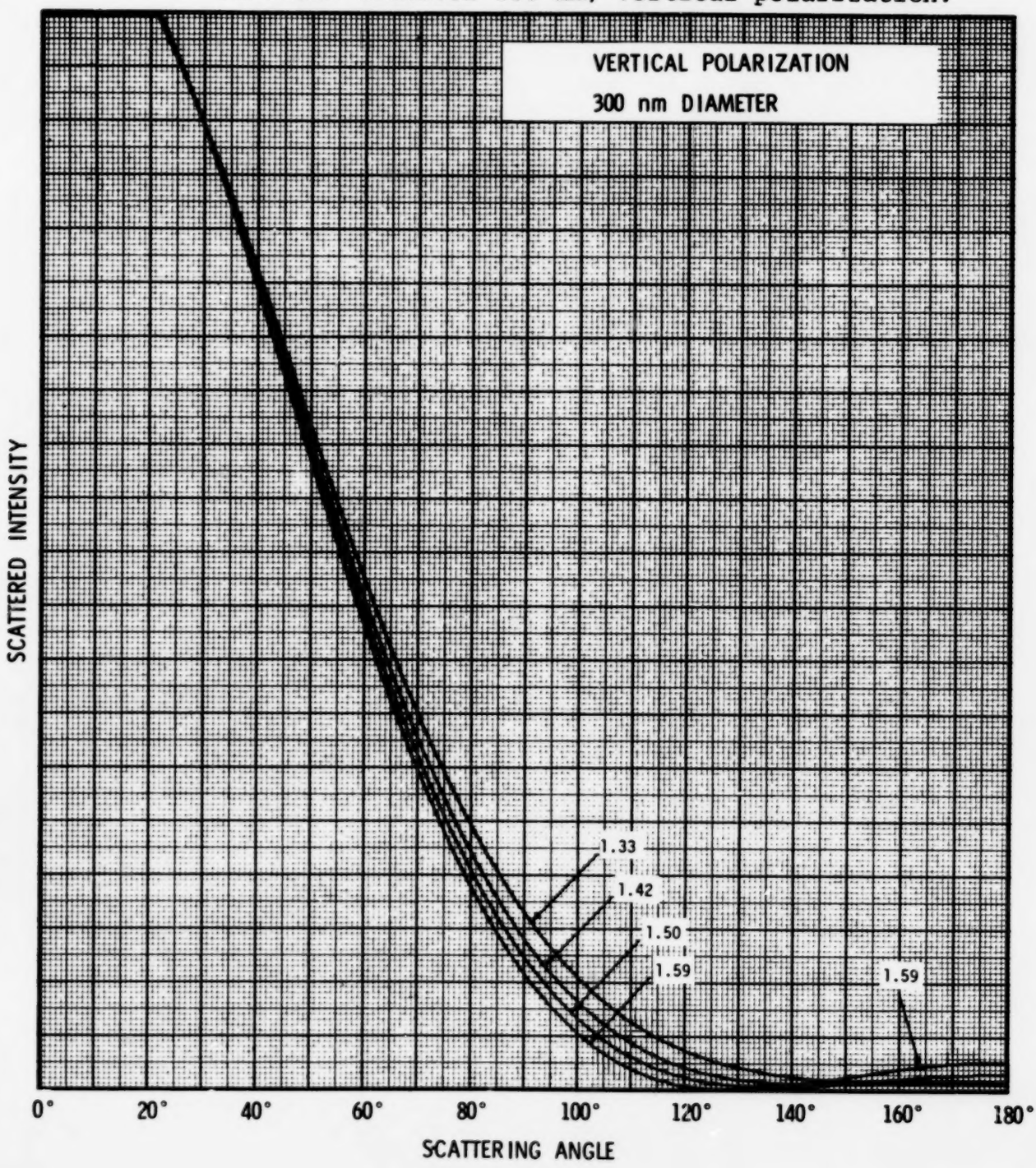


Figure 12 - Theoretical differential scattered intensity for homogeneous spherical particles of refractive indices 1.33, 1.42, 1.5, 1.59 at 514.5 nm wavelength. Particle diameter 300 nm, horizontal polarization.

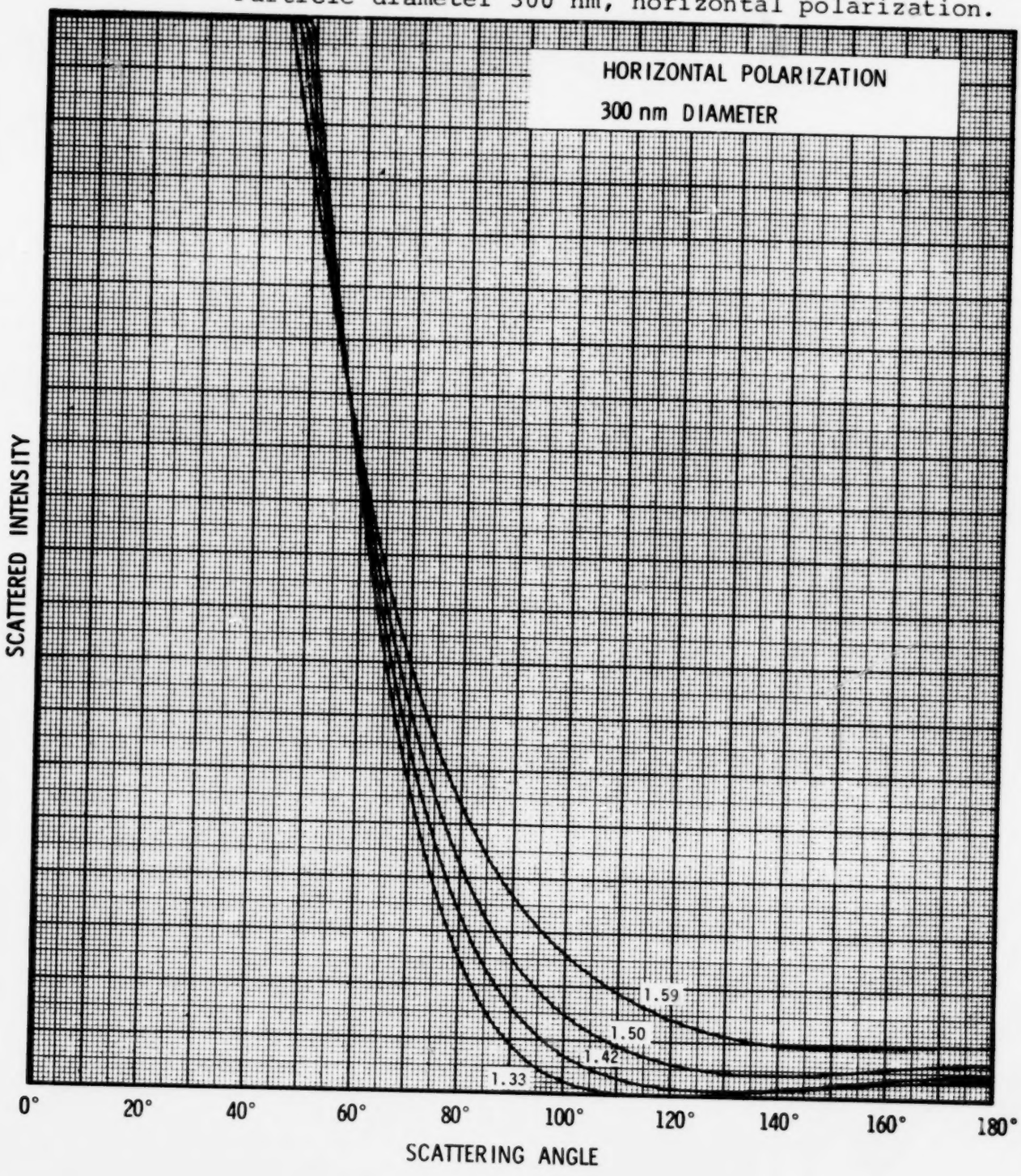


Figure 13 - Theoretical differential scattered intensity for homogeneous spherical particles of refractive indices 1.33, 1.42, 1.5, 1.59 at 514.5 nm wavelength. Particle diameter 500 nm, vertical polarization.

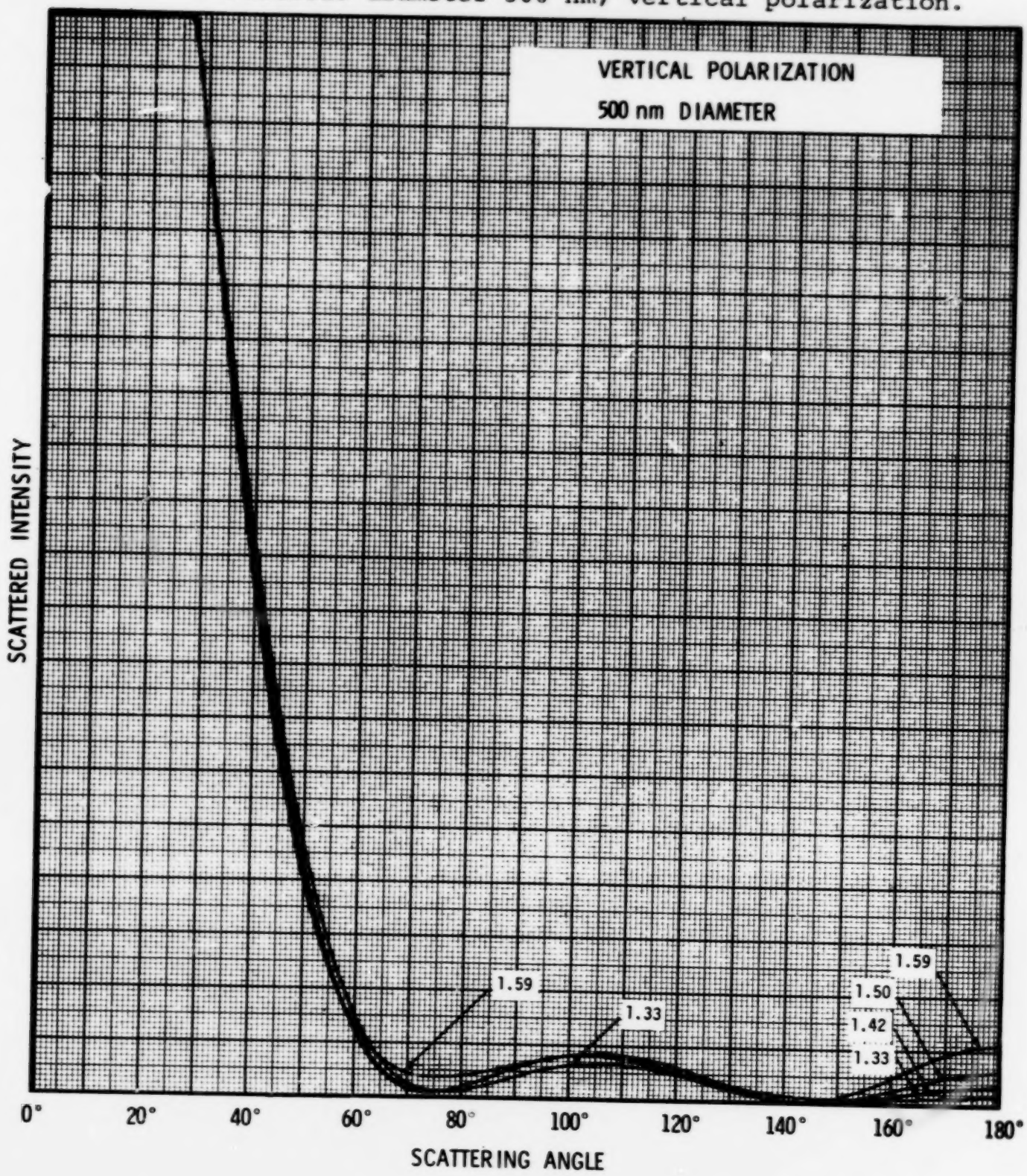


Figure 14 - Theoretical differential scattered intensity for homogeneous spherical particles of refractive indices 1.33, 1.42, 1.5, 1.59 at 514.5 nm wavelength. Particle diameter 500 nm, horizontal polarization.

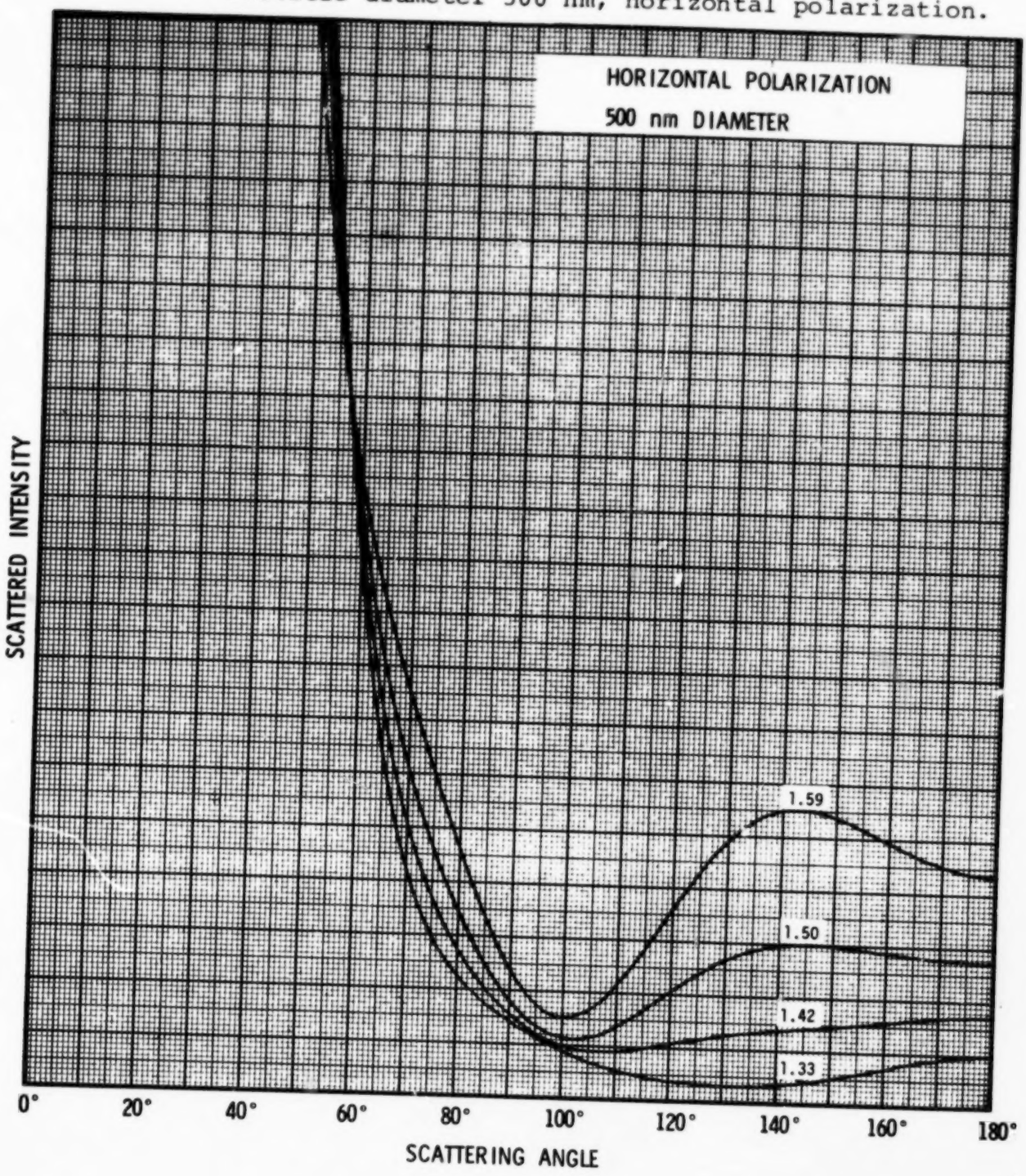


Figure 15 - Theoretical differential scattered intensity for homogeneous spherical particles of refractive indices 1.33, 1.42, 1.5, 1.59 at 514.5 nm wavelength. Particle diameter 1,000 nm, vertical polarization.

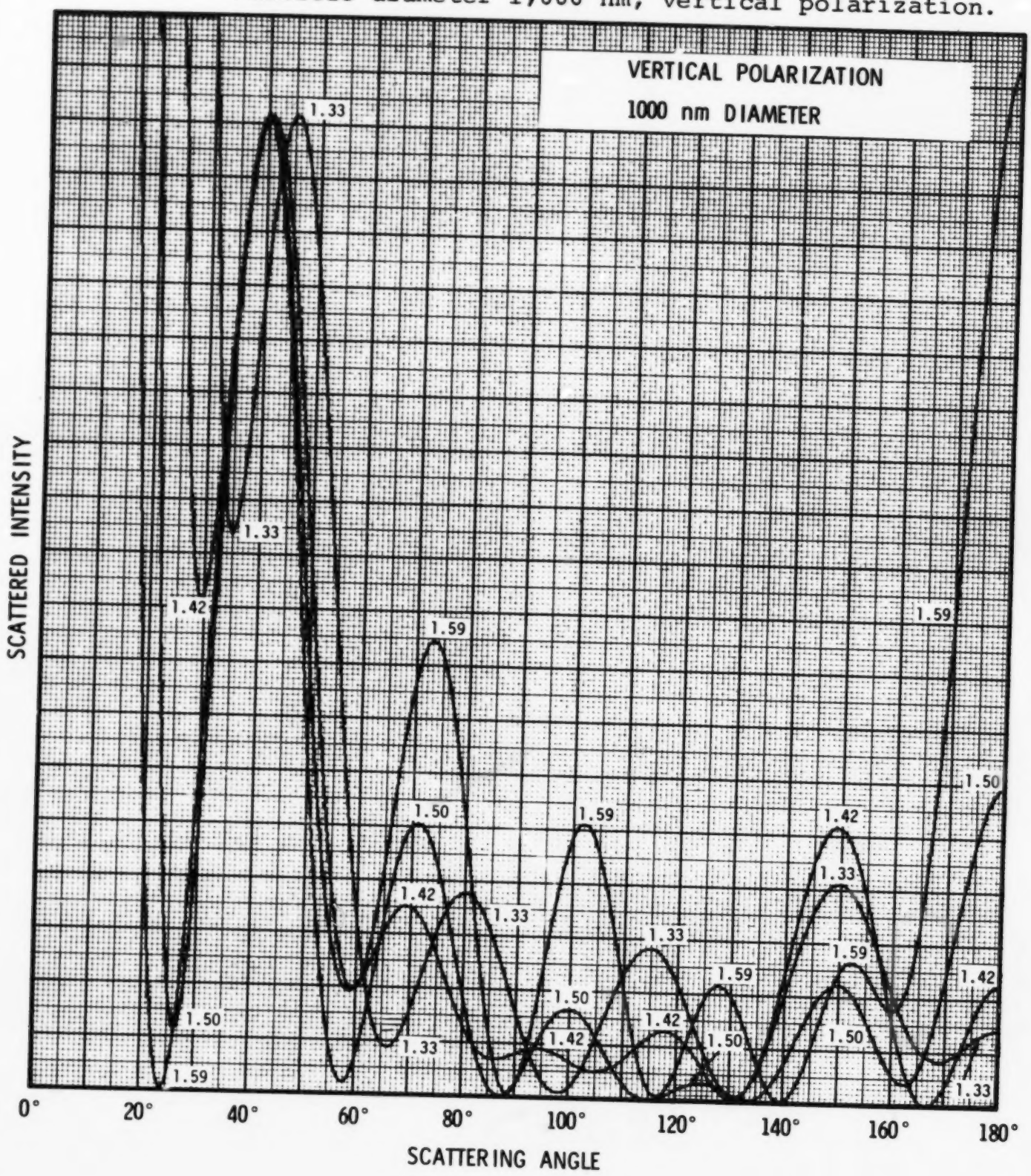


Figure 16 - Theoretical differential scattered intensity for homogeneous spherical particles of refractive indices 1.33, 1.42, 1.5, 1.59 at 514.5 nm wavelength. Particle diameter 1,000 nm, horizontal polarization.

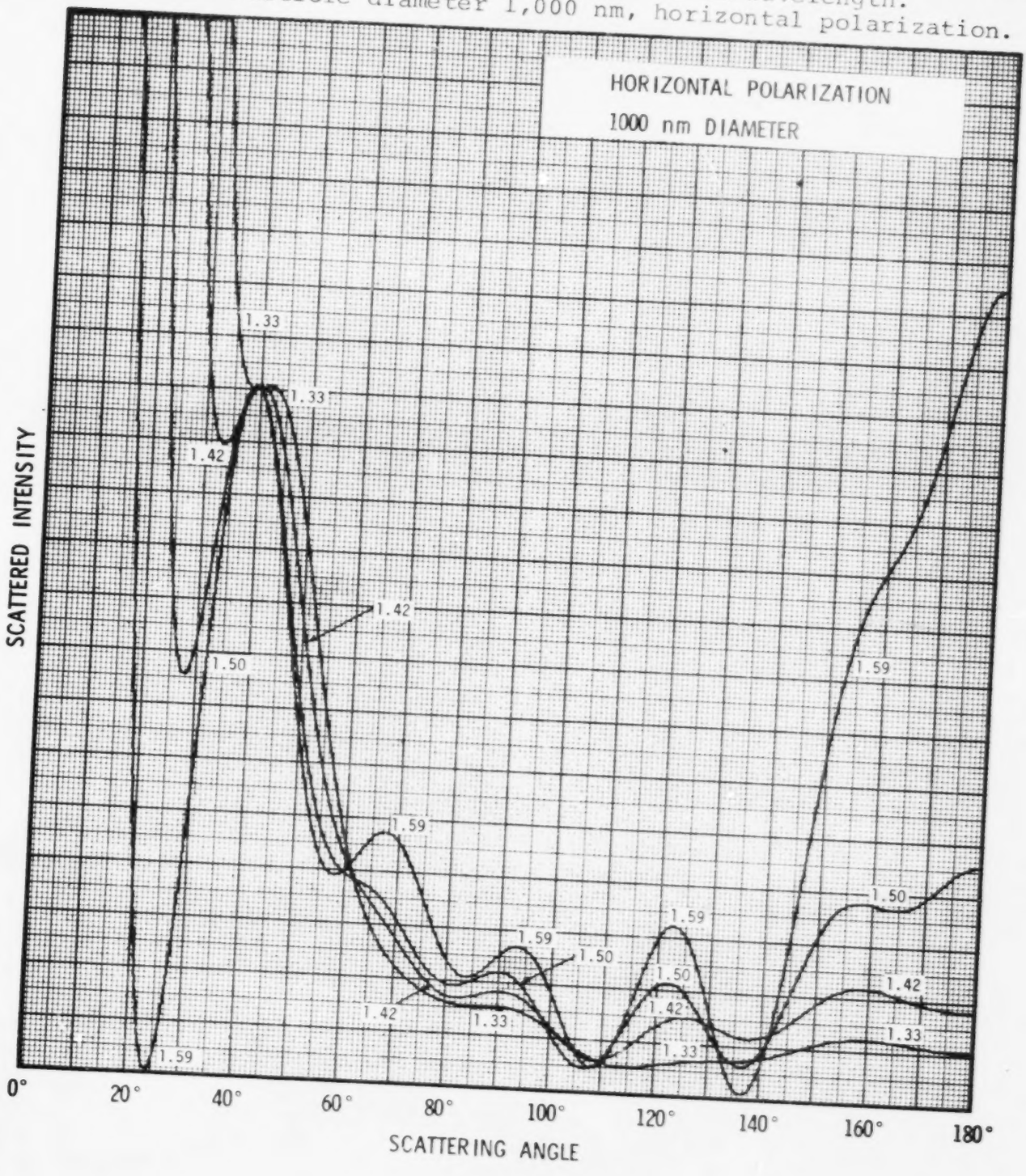


Figure 17 - Particle radius and refractive index as a function of the scattered intensity at 20° and the ratio of the scattered intensity at 40° to that at 20°. Precise absolute measurement of scattered intensity at 20° and 40° allows the determination of radius and index over a limited size range.

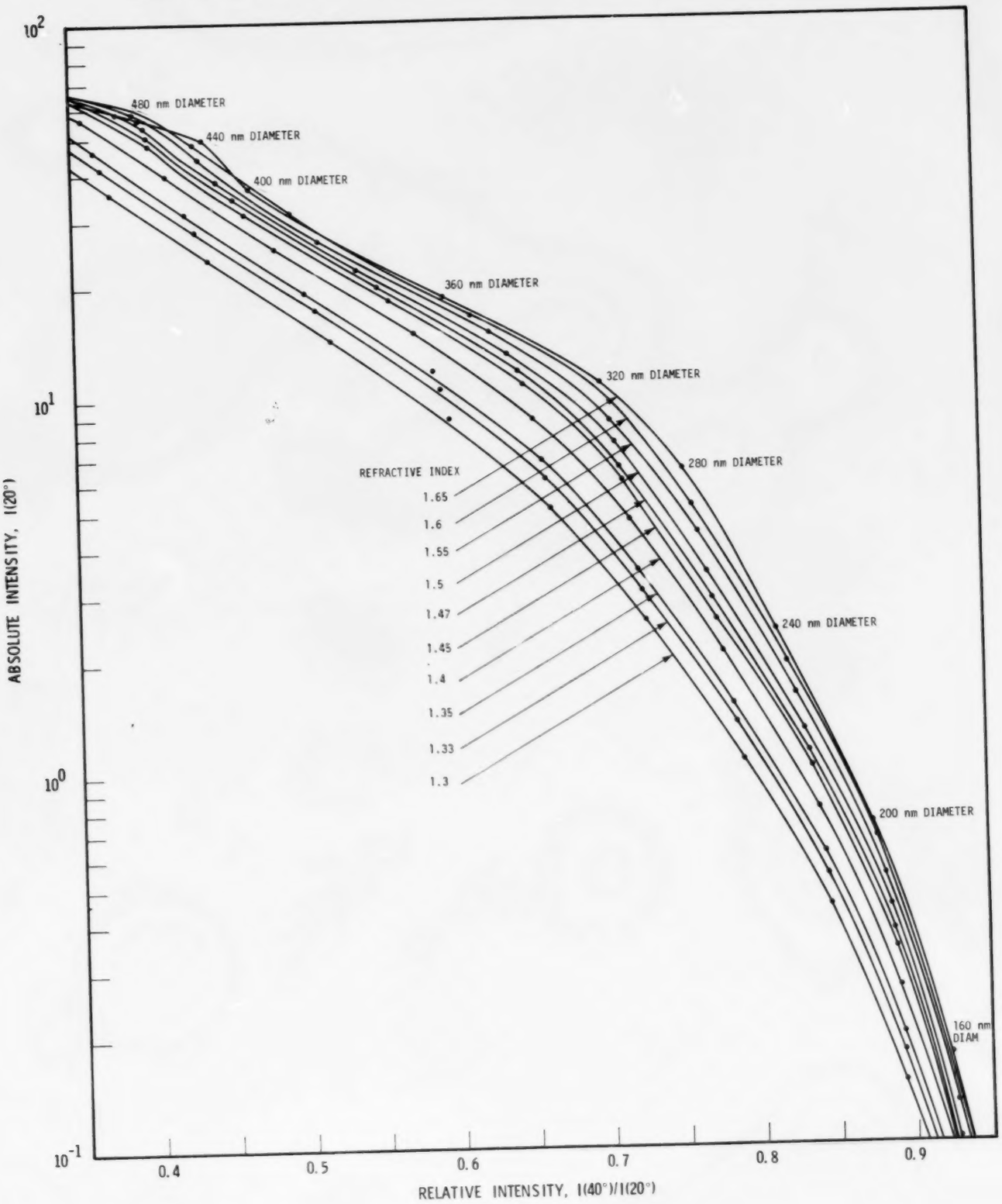
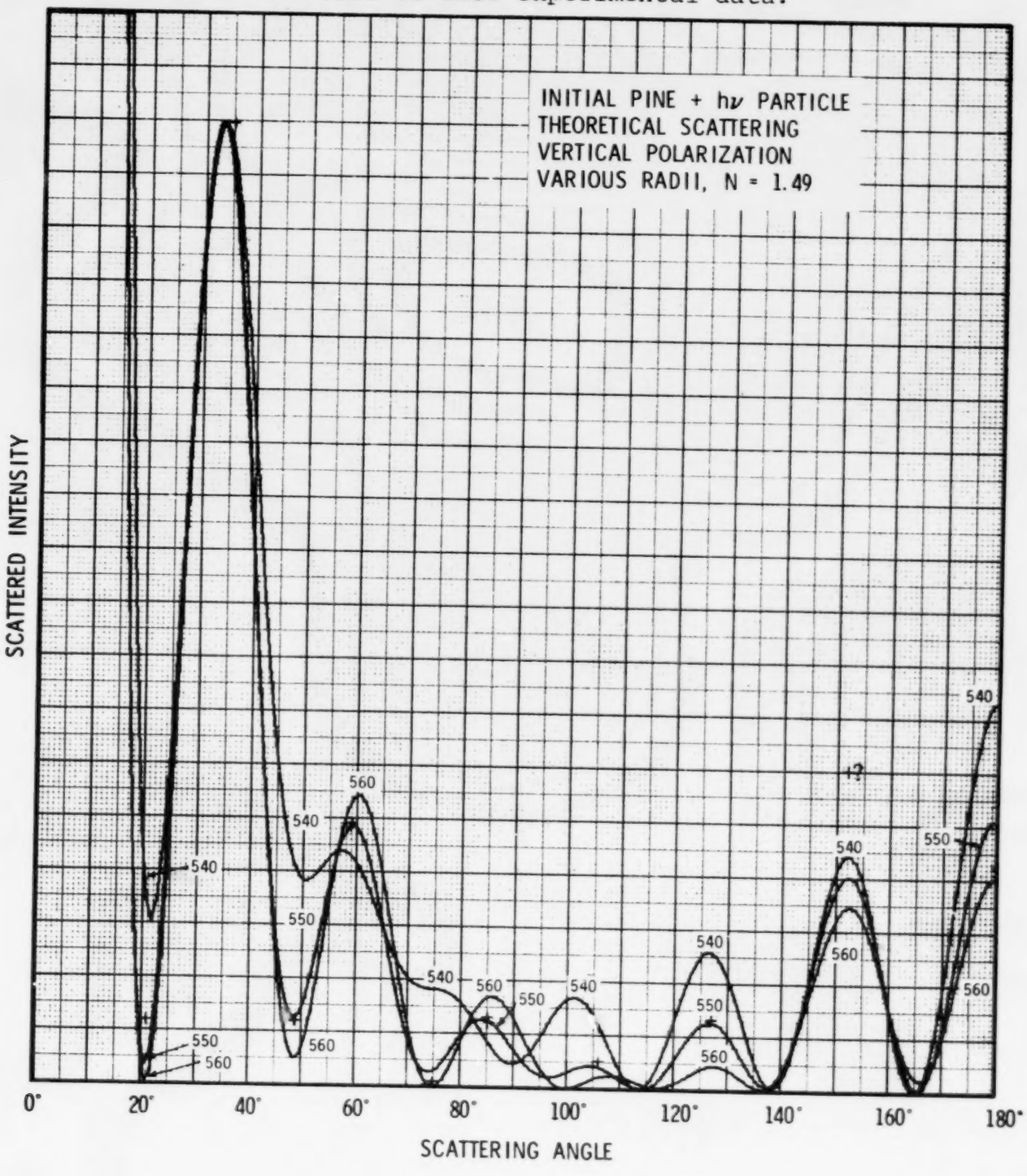


Figure 18 - Theoretical differential scattered intensity for the initial pine aerosol particle (Fig. 2), 514.5 nm wavelength, vertical polarization. n = 1.49 nm; r = 540 nm, 550 nm, 560 nm. Crosses show experimental data.

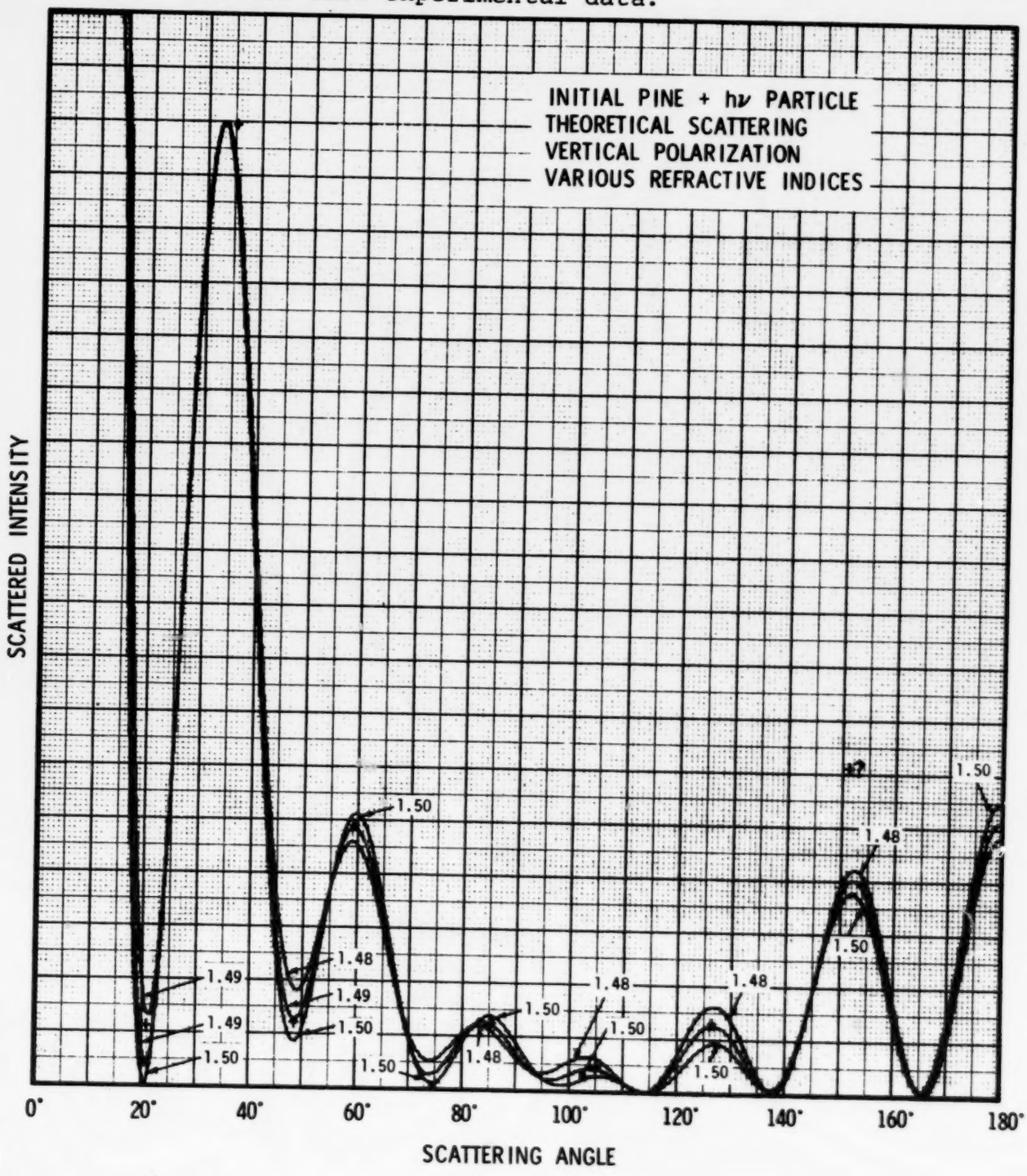


The theoretical scattering curves show that particles smaller than 500 nm diameter exhibit no secondary scattering peaks. As the particle diameter becomes greater than 500 nm secondary scattering peaks in the differential scattering intensity become quite pronounced. For small particles the relative differential scattering intensity is (approximately) a universal function of the parameter nD, where n is the refractive index and D is the diameter. For larger particles the effects of radius and index on the shape of the scattering curve can be distinguished. For particles of diameter smaller than 500 nm, a relative scattering intensity measurement is not adequate to determine the refractive index. However, the absolute value of scattering intensity depends on higher powers of refractive index. Thus the shape of the scattering curve *and* its absolute intensity together provide a unique determination of radius and index for small dielectric spheres. The ratio of the intensity of vertically polarized scattered light at 40°, I(40°), to the intensity at 20°, I(20°), has been found to provide a convenient measure of the shape of the scattering curve. The relation of I(20°) and I(40°)/I(20°) to radius and index is shown in Figure 19 by curves for various values of refractive index with particle radius as a running parameter. Using this figure, a particle radius and an index of refraction can be determined for a measured pair I(20°) and I(40°)/I(20°).

This method of analysis required highly accurate measurements and absolute intensity calibration of the instrument. To be useful in categorizing hydrocarbon aerosols, the index must be determined to approximately one per cent. This requires measurement of the ratio of the intensities at two angles to approximately 0.2% accuracy. The requirement for the absolute intensity measurement is somewhat less, about 1%. Absolute calibration can be carried out using Dow latex spheres as a standard. Measurements to the required accuracy are difficult but are believed to be achievable. Since the accuracy of optical measurements are ultimately limited by the number of photons detected, an increase in laser power will be very helpful for the smaller particles. Since many natural haze particles are smaller than 500 nm diameter, and this approach shows promise for particle identification in this size range, effort to achieve such measurements should be continued. Furthermore, since intensity measurements of only two angles are needed the analysis is compatible with a rapid particle counting and sorting requirement.

For particles of diameter greater than about 500 nm, the determination of radius and refractive index can be based entirely on the vertical and horizontal scattering curves, without absolute intensity calibration. This method has been previously reported.[2] Visual comparison of the measured scattering curves with an atlas of theoretical curves allows the approximate determination of radius and refractive index.

Figure 19 - Theoretical differential scattered intensity for the initial pine aerosol particle (Fig. 2), 514.5 nm wavelength, vertical polarization. r = 550 nm; n = 1.48, 1.49, 1.50. Crosses show experimental data.



Then a net of curves with closely spaced value of radius and index are computed in the neighborhood of the measured particle. Careful examination of the number and position of the peaks and valleys, and particularly the relative height of the peaks and valleys allows selection of the fit. Theoretical curves bracketing the best fit for the representative Pine + UV particle (Figures 2 and 3) and the representative Gasoline + NO_x + UV particle (Figure 4) are shown in Figures 20 through 25. Considerable theoretical and experimental attention has been given to the uniqueness of size and index determinations by light scattering by other workers.[3,4]

Further development of analytical techniques will be required for an easily automated index measurement for large particles. However, since these curves have characteristic properties recognizable by eye, it seems probable that analytical methods could be developed which would provide a rapid and accurate determination of refractive index and radius for large spherical particles. Fourier, or spherical harmonic analysis, promise to offer a more systematic approach to this problem. The measurement of absolute intensities required for smaller particles may also be of use in this size range. More theoretical work is needed in this area.

Figure 20

Theoretical differential scattered intensity for the initial pine aerosol particle (Fig. 2), 514.5 nm wavelength, horizontal polarization. n = 1.49; r = 540 nm, 550 nm, 560 nm. Crosses show experimental data.

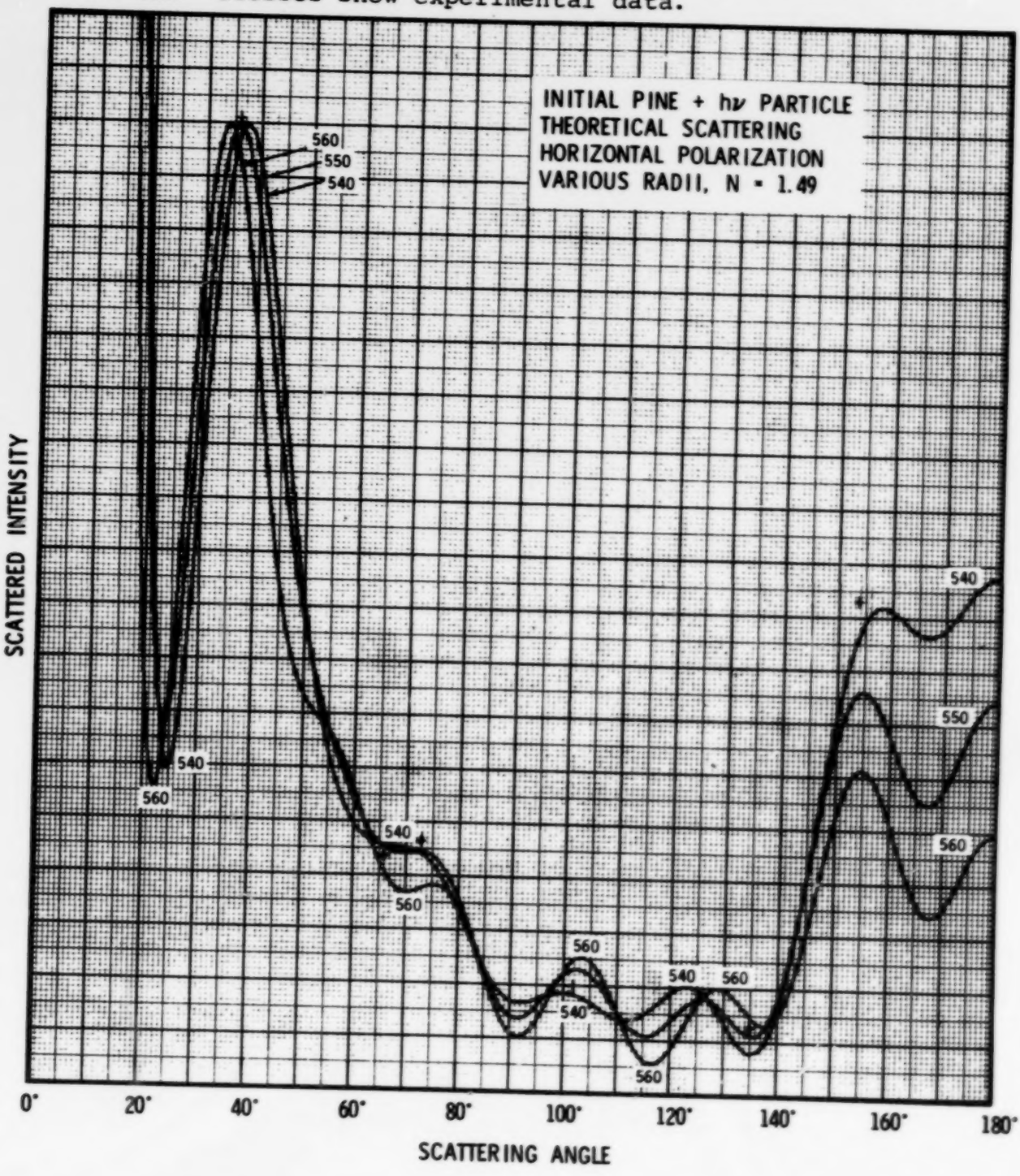


Figure 21
Theoretical differential scattered intensity for the initial pine aerosol particle (Fig. 2), 514.5 nm wavelength, horizontal polarization. r = 550 nm; n = 1.48, 1.49, 1.50. Crosses show experimental data.

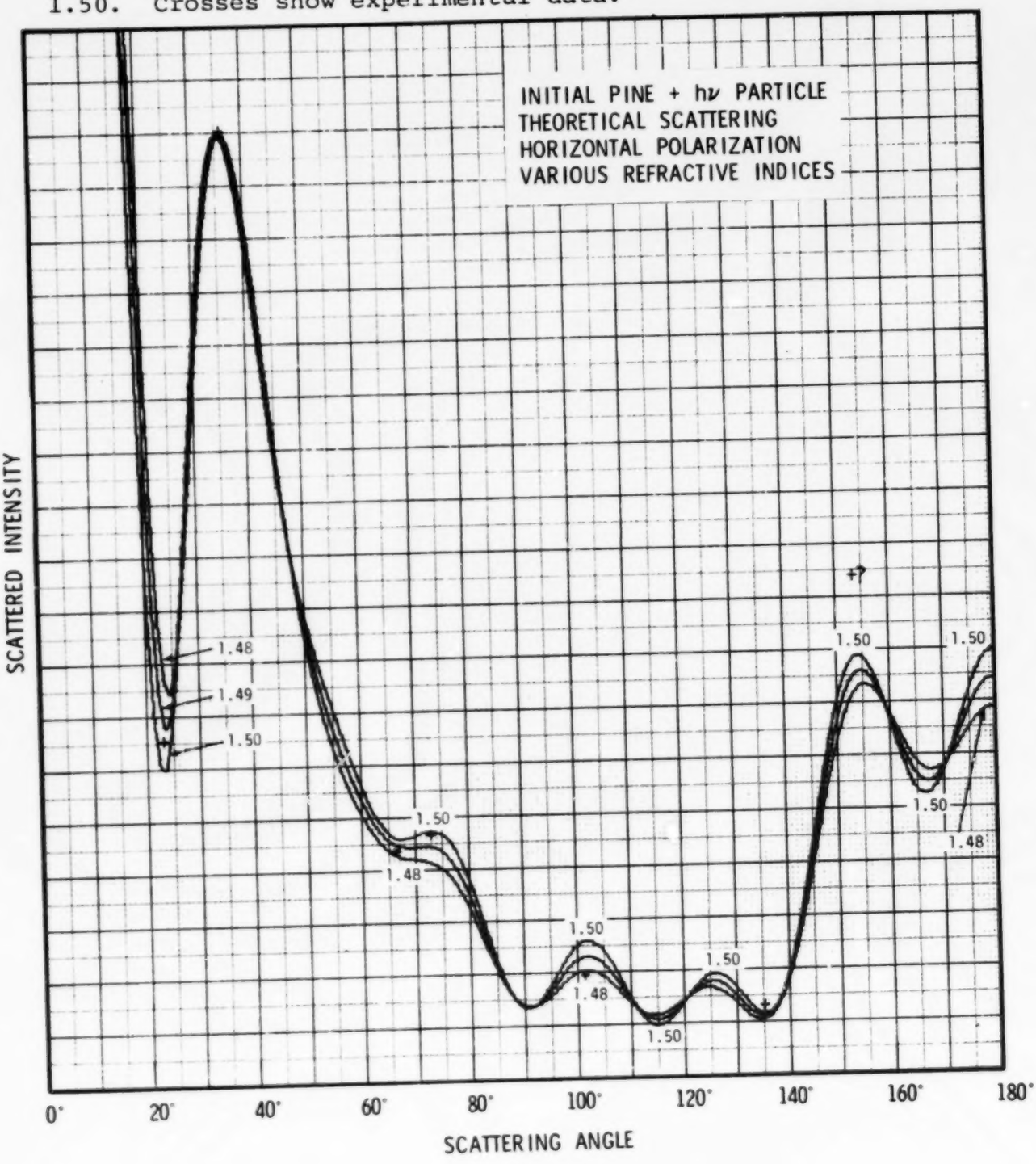


Figure 22

Theoretical differential scattered intensity for the 90-minute pine aerosol particle (Fig. 3), 514.5 nm wavelength, vertical polarization. n = 1.49; r = 495 nm, 505 nm, 515 nm. Crosses show experimental data.

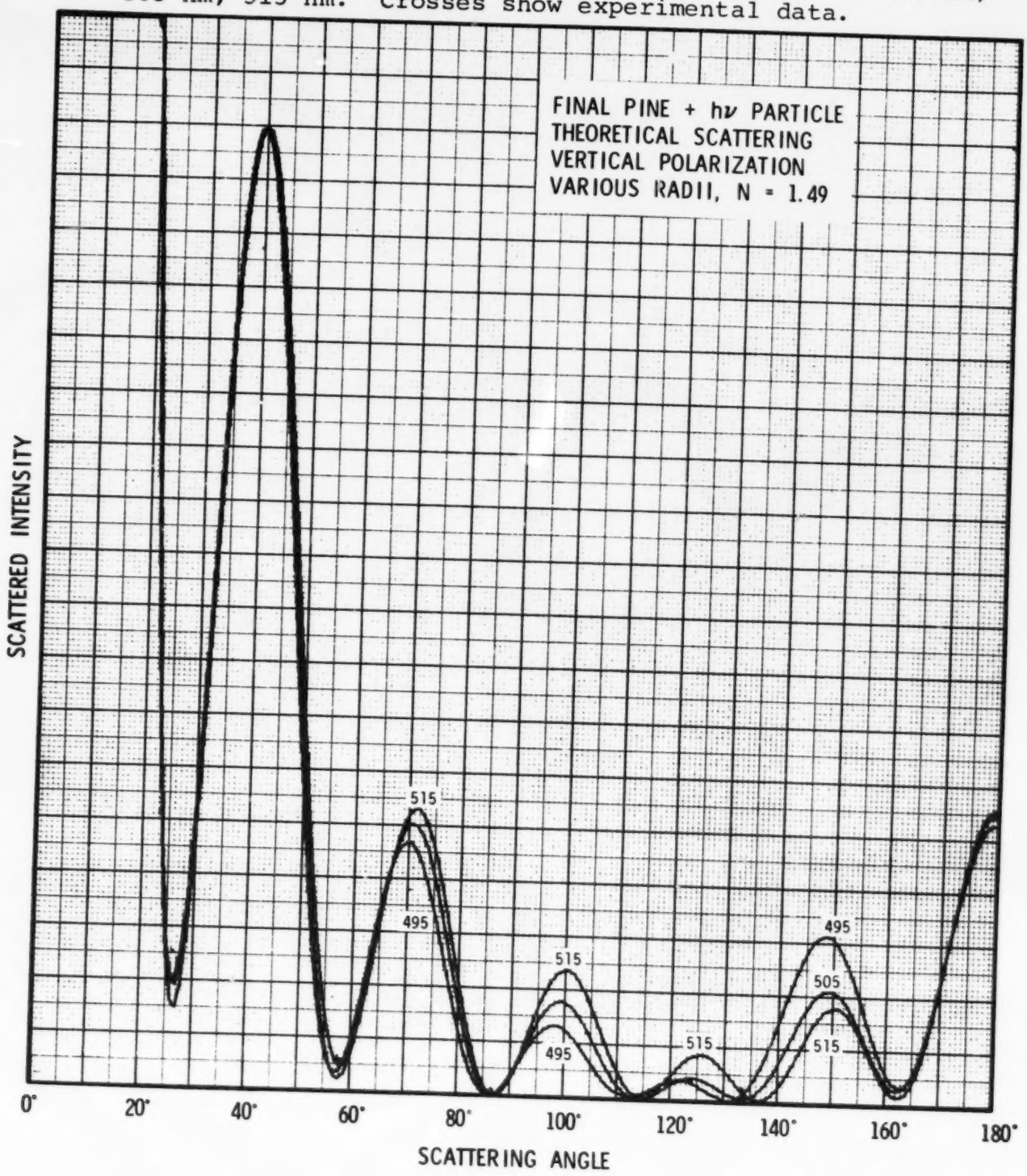


Figure 23
Theoretical differential scattered intensity for the gasoline + NO_x aerosol particle (Fig. 4), 514.5 nm wavelength, vertical polarization. n = 1.54; r = 400 nm, 410 nm, 420 nm. Crosses show experimental data.

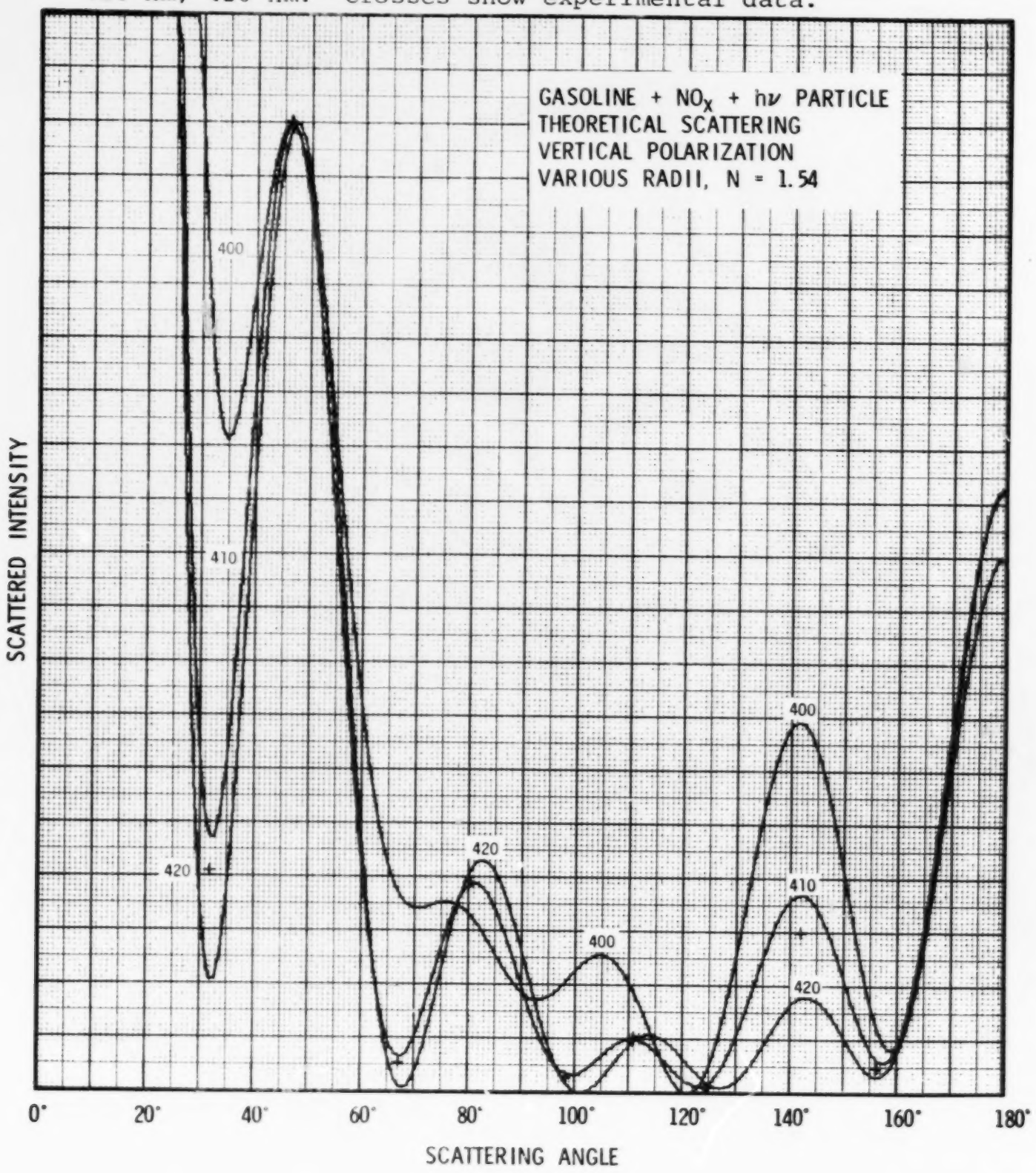


Figure 24

Theoretical differential scattered intensity for the gasoline + NO_x aerosol particle (Fig. 4), 514.5 nm wavelength, vertical polarization. r = 410 nm; n = 1.52, 1.54, 1.56. Crosses show experimental data.

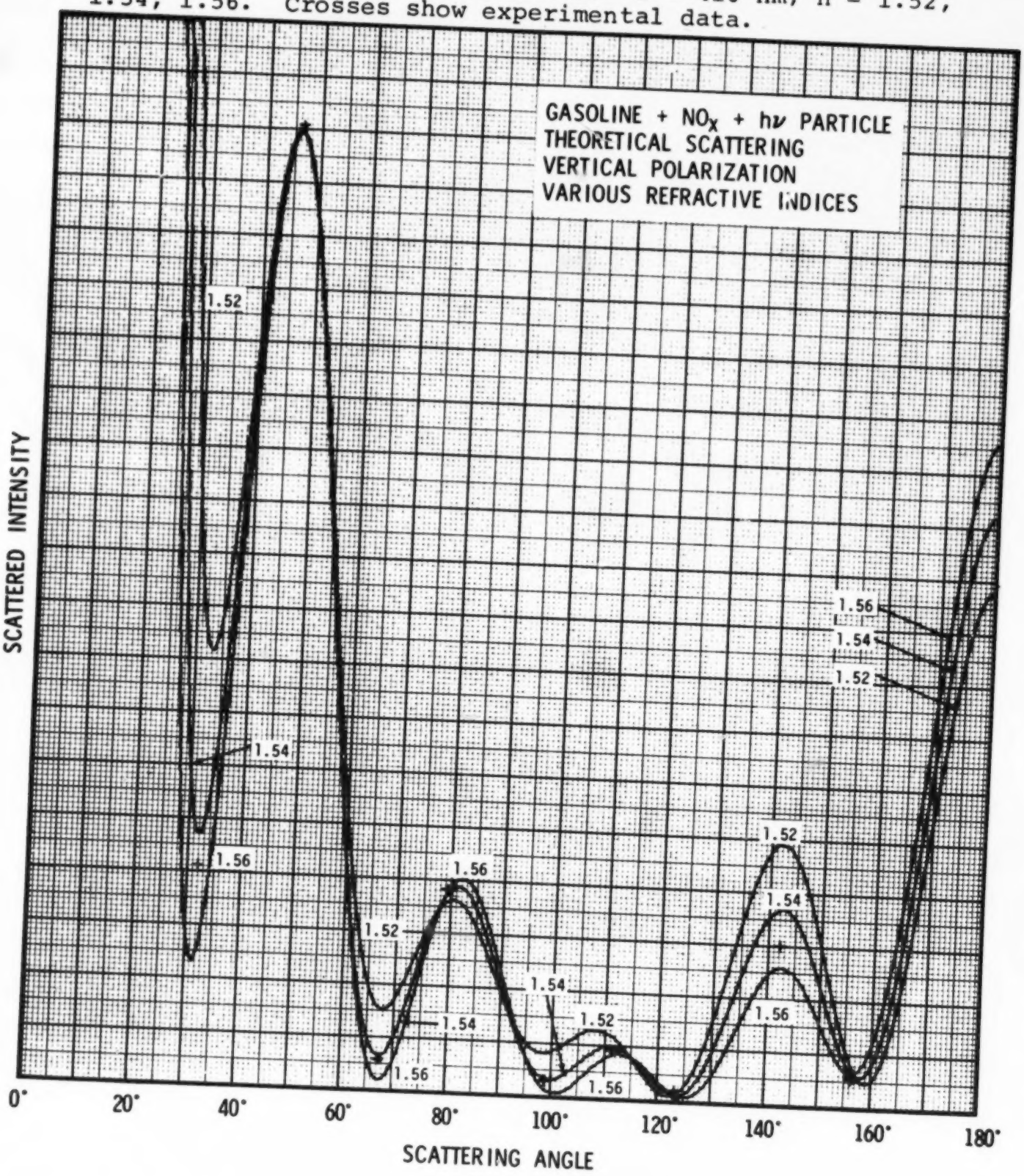


Figure 25 Theoretical differential scattered intensity for the gasoline + NO_x aerosol particle (Fig. 4), 514.5 nm wavelength, vertical polarization. n = 1.54; r = 400 nm, 410 nm, 420 nm. Crosses show experimental data.

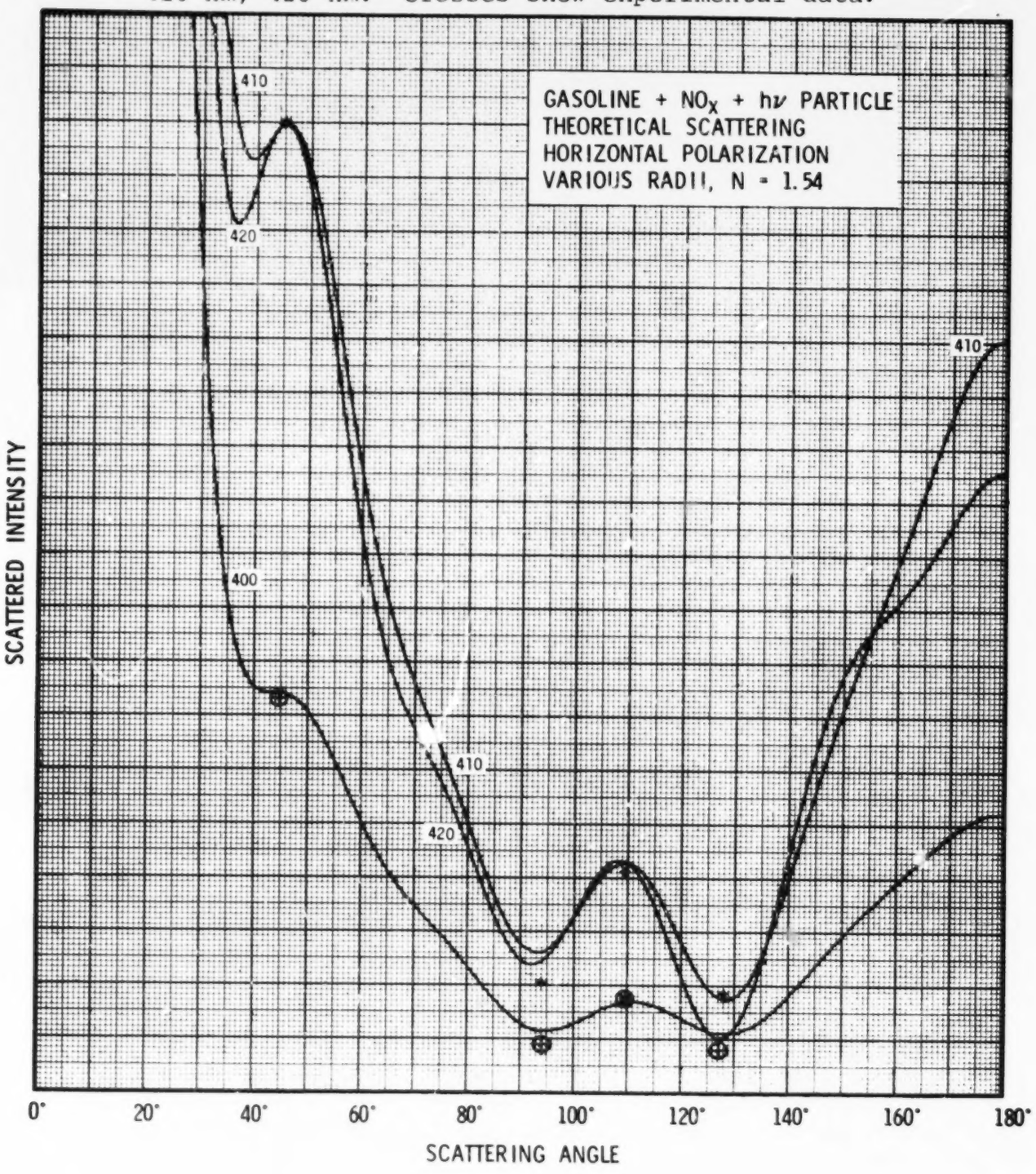
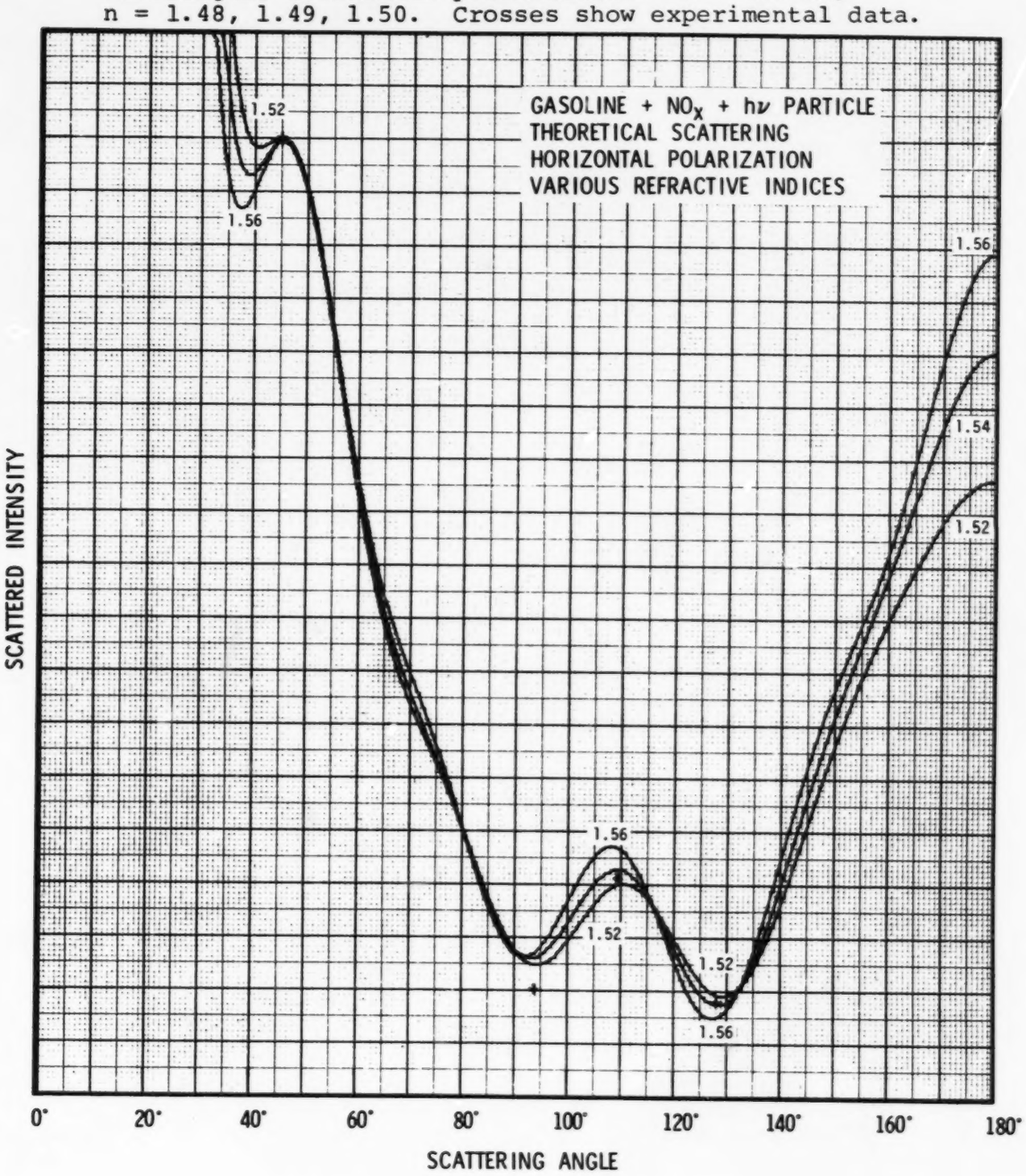


Figure 26
Theoretical differential scattered intensity for the gasoline + NO_x aerosol particle (Fig. 4), 514.5 nm wavelength, horizontal polarization. r = 410 nm; n = 1.48, 1.49, 1.50. Crosses show experimental data.



4. CONCLUSIONS AND DISCUSSION

Reaction chamber aerosol single particle light scattering measurements have been used to determine the refractive indices of pine + UV and gasoline + NO_x + UV. The values obtained are 1.49 ± .01 and 1.54 ± .02, respectively. Thus these aerosols can be distinguished by single particle optical scattering measurements. Differential light scattering intensity measurements of single atmospheric haze particles have been made successfully in the Santa Barbara and Los Angeles areas.

It appears feasible to use such measurements to distinguish the origin of certain classes of individual atmospheric haze particles. More extensive field studies are required to properly evaluate the usefulness of the method. Joint chemical and light scattering studies would be particularly useful.

An analytical method to determine the refractive index of particles in the 100 to 500 nm diameter range by using absolute intensity of the scattering at two fixed angles has been developed. By adjusting the angles of measurement the method can be extended to smaller or larger particle diameters. This promises to be an effective tool, well adapted for rapid measurements of large numbers of particles, for air pollution studies.

Nonspherical particles have been observed in automotive exhaust samples. Such particles are expected to change the polarization of the scattered light. This readily observable effect offers a potentially powerful but untested tool for the categorization of particles. Also, an unsymmetric particle does not scatter light with equal intensity at equal scattering angles on opposite sides of the incident beam as a spherical particle does. Measurement of the correlation of the signals in opposed detectors would provide additional information about the symmetry of the scatterer. Flicker amplitude measurements may also be useful.

The speed limitations of chart recorders and the manual manipulation of single particles are not inherent in the light scattering measurement. Once the utility of scattering measurements has been proven, the use of special purpose computers and high speed scattering detectors can make the routine measurement of airborne particles a convenient and precise tool.

5. REFERENCES

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